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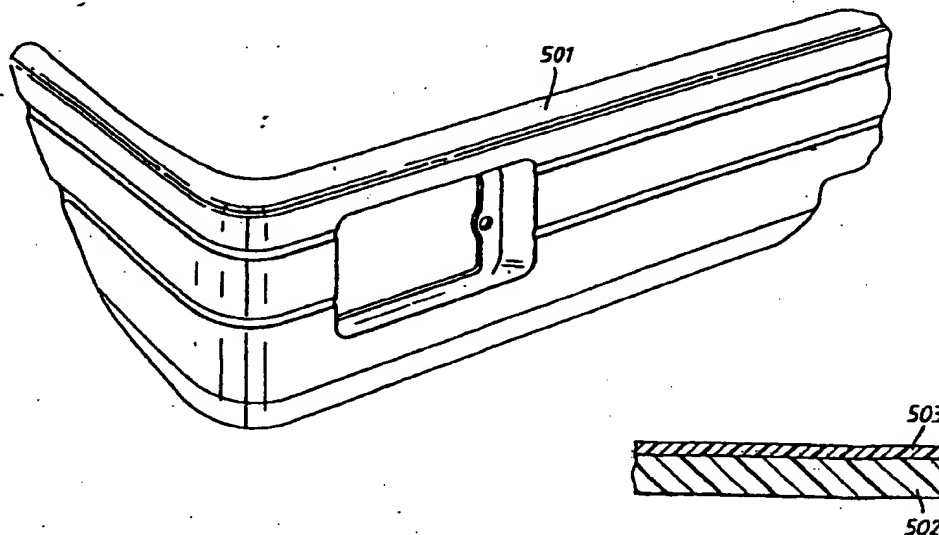
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<p>(21) International Application Number: PCT/GB93/01997</p> <p>(22) International Filing Date: 23 September 1993 (23.09.93)</p> <p>(30) Priority data: 9220207.6 24 September 1992 (24.09.92) GB 9305708.1 19 March 1993 (19.03.93) GB 9305709.9 19 March 1993 (19.03.93) GB</p> <p>(71) Applicants (for all designated States except US): H.B. FULLER COMPANY [US/US]; 2400 Energy Park Drive, Saint Paul, MN 55108 (US). ROVER GROUP LIMITED [GB/GB]; International House, Bickenhill Lane, Bickenhill, Birmingham B37 7HQ (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): DODD, Keith, Herbert [GB/GB]; 5 Parsons Drive, Richmond Park, Gnosall, Staffordshire ST20 0QS (GB). EASTERLOW, Ronald, Arthur [GB/GB]; 312 Broad Lane, Coventry CV5 7AT (GB). SMITH, Gordon, Frederick [GB/GB]; 5 The Maples, Bedworth, Nuneaton, Warwickshire CV12 0BE (GB). STEPHENSON, Peter, John [GB/GB]; 21 Ettington Close, Wellesbourne, Warwick CV35 9RJ (GB). WELTON, Nicolas, Jason [GB/GB]; 141 Kingshurst Road, Northfield, Birmingham B31 3LJ (GB).</p>	<p>(74) Agents: CARTER, Caroline, Ann et al.; Abel & Imray, Northumberland House, 303-306 High Holborn, London WC1V 7LH (GB).</p> <p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), ES, FI, FI (Utility model), GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, SK (Utility model), UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	

(54) Title: THERMOPLASTIC COATED SUBSTRATES



(57) Abstract

A polymeric article, for example, a vehicle component, comprises a thermoplastic coating layer, for example a paint layer or an electrically conductive layer, on a thermoplastic substrate, which may comprise recycled material. The article, which may be recyclable by melt-processing techniques, may be prepared by an in-mould coating process in which a solid thermoplastic paint or other coating material, in softened or molten form, is applied to a mould surface before, or substantially simultaneously with, introduction of thermoplastic substrate material into the mould. Thermal spraying, multiple-injection and blow moulding methods for making the articles are described.

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THERMOPLASTIC COATED SUBSTRATES.

The invention relates to articles comprising coated substrates, more especially polymeric substrates having a coating, for example, a decorative and/or protective coating, thereon, and to methods of manufacturing such articles. The invention has particular, but not exclusive, relevance to coated plastics parts for use in the automotive industry.

Traditionally, the production of coated, especially painted, polymeric substrates has almost exclusively involved the application of solvent-based coating materials to preformed substrates. Many methods can be used for applying coatings from solution, for example, spraying or dipping of substrates, and solvent-based coating materials can be used with many different types of substrate.

Where a solvent-based coating is applied to a product such as a moulded plastic article, coating is carried out as a separate step after the article has been moulded, usually in a special area dedicated to that purpose. In such an area it is possible to obtain good control over coating quality, and to control, for example, levels of dust and solvents. The last-mentioned point is particularly important in view of recent environmental legislation in relation to the control of emissions and disposal of organic solvents. The use of separate coating steps in special coating areas can, however, add significantly to production costs by, among other things, reducing production rates.

Proposals have also been made for the production of coated polymeric articles by applying the coating in sheet or powder form to the preformed substrate. It has further been proposed to position preformed sheets of the coating material in the mould in which the article is to be formed. Thus, for example, JP 55 133920A discloses

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the manufacture of a container, suitable, for example, for use as the fuel tank of a vehicle, by forming a number of container parts of, for example, a polyolefin and applying nylon in sheet or powder form to the parts to form a barrier layer, and then welding the parts to form the container. In another embodiment, a sheet of the barrier material is applied to a surface of a mould of an injection moulding machine used to mould the container parts. In EP 376 010A, which emphasises the difficulty of painting plastic exterior body parts for use in the automotive industry, a coated metal veneer is used to provide a plastic body part with an outer surface having, for example, high gloss and durability. US 4 943 680 also refers to the difficulty of providing a painted finish on plastic automobile parts, and proposes bonding a flexible sheet material to the part to be painted, the flexible sheet material comprising a clearcoat layer and a pigmented layer. The bonding step may be carried out in a mould.

Because the above methods involve the use of solvent-based coating materials and/or the production of a coating layer in a separate step, there has recently been interest in in-mould powder coating methods in which a coating and a substrate are shaped in the same mould. In such in-mould powder coating methods, the coating material in powdered form is typically used to cover the inside of the mould before the substrate is moulded. Coating of the mould is normally effected by electrostatic spraying.

Numerous proposals have been made for in-mould powder coating methods of the type referred to above. Examples of such proposals are indicated below.

EP 461 320A discloses a thermosetting powder particularly suitable for use with fibre-reinforced plastics. The powder provides, after curing, an article comprising an electrically conductive primer layer on a

substrate, the primer layer facilitating subsequent painting by, for example, electrostatic paint spraying.

EP 309 088A describes the use of a powdered unsaturated polyester resin formulation for use in the production of coated reinforced polyester articles. The powder is applied to a heated mould surface, the molten substrate material is introduced into the mould, and the whole system is cured, giving crosslinking between the coating and the substrate.

EP 98 655A discloses coating a heated mould with a powdered unsaturated polyester resin, in admixture with a hardening agent, prior to the introduction of the substrate material. The mould walls have a temperature of 80 to 180°C so that partial curing of the coating material takes place before introduction of the substrate material which may be, for example, a fibre-reinforced hardenable unsaturated polyester.

US 4 681 712 discloses a moulding process which comprises electrostatically coating the inner surface of a mould with a powdered resin composition and then introducing a plastic substrate material into the mould.

JP 61 220813A discloses the formation of a coating on a plastic moulding by electrostatically coating the cavity surface of a mould with a resinous powder which is electrically conductive or capable of absorbing electromagnetic energy, electrostatically coating the coated surface with another powdered resinous composition, and introducing plastic material into the mould so that the resinous composition is heated by the plastic material.

There have also been proposals for forming a coated product by the injection of a coating material and a substrate material into the same mould.

GB 1 156 217 relates to the production of injection moulded articles having a foamed core and an unfoamed surface skin, the object being to provide a skin

substantially free of the sink marks and voids which tend to appear unless an unfoamable resin is used to form the skin. GB 1 338 647 relates to the production of acoustically damped articles comprising a relatively thick unfoamed skin on a foamed core.

GB 2 080 187 A discloses an injection moulding method in which a coating material is forced into a mould using a plastic substrate material of higher viscosity. Paints in liquid form and liquid thermosetting resins are mentioned as coatings for thermosetting substrate materials.

A further proposal, reported on pages 4, 5, 8 and 11 of "British Plastics and Rubber", March 1992, involves using an injection moulding machine which comprises two injection units, one injection unit being used to inject molten material for forming a skin, following which molten material for forming the body of the article is injected using the other injection unit. Skins formed in such a manner typically have a thickness of several millimetres. In another proposal, as reported on pages 42 and 43 of "Modern Paints and Coatings", July 1990, molten material for forming the coating is injected after injection of the molten material for forming the body of the article, and the two materials are then cured.

EP 392 571 A relates to laminated preforms which can subsequently be used for forming blow moulded articles. The preforms, which are formed by injection moulding, contain intermediate layers the thickness of which is reduced during blow moulding, thus making it possible to obtain, for example, laminates containing thin barrier layers.

The previously proposed coatings and coating methods are satisfactory in some situations, but not all. Thus, for example, in many industries, it would be desirable to be able to make articles from tough, durable thermoplastic materials such as polypropylene. For

instance, polypropylene would be very useful for making articles such as car bumpers and other components of vehicles if it could be painted simply and at a reasonable cost, and there are many other circumstances where it would be desirable to provide a thermoplastic material with a surface coating which differs in appearance and/or properties from the bulk of the material. Previous proposals for making coated substrates comprising thermoplastic materials such as polypropylene did not, however, give products obtainable at reasonable cost with a high quality durable surface finish.

In a first aspect, the present invention provides an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, the coating comprising a thermoplastic reversibly crosslinkable polymeric material. Advantageously, the reversibly crosslinkable polymeric material is an ionomer or a thermoplastic elastomer.

The invention also provides an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, the coating having a thickness of at most 500 μm and comprising a thermoplastic polymeric material and one or more substances selected from finely divided metallic materials (as hereinafter defined), finely divided pearlescent materials, and UV stabilizers, with the proviso that the coating does not form part of a sheet of material which has been brought as such into contact with the substrate. Advantageously, the coating is not a sheet of material which has been brought as such into contact with the substrate.

The present invention further provides an article comprising a substantially thermoplastic substrate comprising recycled material, the substrate having a

substantially thermoplastic coating of thickness at most 1 mm on at least one surface thereof.

In this specification the term "recycled material" means material derived from complete articles rejected after their manufacture as being off specification, and/or material derived from articles salvaged after use. Such used articles are preferably articles in accordance with the invention. (The articles of the invention, which are of composite structure, comprising a substrate and a coating, can if desired be completely recyclable.) Recycled material in accordance with the invention may comprise one or more thermoplastic polymeric materials, at least one of which thermoplastic materials may if desired be derived from scrap material from the manufacturing process used in making articles in accordance with the invention. Recycled material may also contain material that is infusible at the processing temperatures used, provided that the infusible material is in such a form that it does not interfere with the processing steps or with the properties of the final product.

The article of the invention may be made by any suitable method, for example, a process in which the substrate and coating are shaped in the same mould, or a coextrusion process. Examples of suitable processes for use in making the articles are injection moulding, compression moulding, blow moulding and coextrusion processes, and combinations of those processes. The article may have any desired form. In one advantageous embodiment of the invention, the article is made by a process in which the substrate and coating are shaped in the same mould and is in the form of a vehicle component. In another advantageous embodiment of the invention, the article is made by a coextrusion method and may be, for example, in the form of a frame, for example, a window frame, a cable comprising at least two layers comprising

thermoplastic material, or a fibre. Details of methods suitable for making an article of the invention are given later in this specification.

When the article is made by an in-mould coating process, in which the coating and the substrate are shaped in the same mould, the process is preferably one in which a polymeric material for forming the coating is in softened or molten form when it is brought into contact with the mould surface.

The invention also provides an article comprising a substantially thermoplastic substrate having a coating of thermoplastic paint on at least one surface thereof, the article having been made by a process in which a polymeric material for forming the coating and a polymeric material for forming the substrate are introduced into a mould and shaped in the mould to produce the article, if necessary with the application of heat, the coating material being brought into contact in softened or molten form with a surface of the mould or with the substrate material.

In articles of the invention in which the coating thickness is not an essential feature, the coating advantageously has a thickness of at most 1 mm and preferably at most 500 μm .

The present invention further provides an article comprising a recyclable vehicle component, the article comprising a substantially thermoplastic substrate comprising recycled material, the substrate having a substantially thermoplastic coating, for example, thermoplastic paint coating, thereon. In one embodiment of the invention, both the coating material and the substrate material comprise a propylene homo- or copolymer.

The invention further provides an article according to any of the above statements of invention manufactured by a multiple injection process, and a recyclable vehicle

component which is an article according to any of the above statements of invention and which is made from melt-processable material.

The coating in the article of the invention may, if desired, be a transparent or translucent layer which preferably contains a UV stabilizer and which protects the underlying substrate and/or enhances the appearance and/or properties of the article. Thus, for example, the coating may be a colourless or coloured clearcoat layer. In an advantageous embodiment of the invention, however, the coating is opaque and comprises a polymeric material and a finely divided relatively infusible material which may be, and in many cases is, a pigment. The finely divided material may impart desired properties and/or a desired appearance to the coating. When the coating is opaque, it may if desired be such that a further layer, for example, a clearcoat layer, can be applied over it. (Alternatively, an article comprising a core material, an opaque layer and a clear coat layer may be formed in a single operation using, for example, an injection moulding machine capable of injecting three different materials.)

In an especially advantageous embodiment of the invention, the coating comprises one or more substances selected from pigments, finely divided metallic materials, finely divided pearlescent materials, and UV stabilizers, and the coating forms a thermoplastic paint layer on the substrate. Such a paint layer has, inter alia, the advantage of being applied by a process which does not require the use of solvents for the paint. In particular, articles of the invention, which may be prepared in a single step process using a solvent-free paint which is solid at room temperature, may if desired be abrasion- and weather-resistant and may have a desired appearance, for example, a metallic and/or pearlescent appearance. Further, a high gloss finish may

be obtained, if desired. The articles can thus be such that they do not require a finishing paint coating applied, for example, outside the mould in which they are shaped, although the provision of a further coating on the articles, in particular a clear coating, is not excluded.

In another advantageous embodiment of the invention, the article comprises a coating containing electrically conductive particles which impart electromagnetic shielding characteristics to the coating and thus to the article. Alternatively, or in addition, electromagnetic shielding characteristics may be imparted by the use for the coating of an electrically conductive polymeric material, for example, a polyaniline.

Preferred materials for use in the coatings of articles according to the present invention are discussed in greater detail later in this specification.

It will be appreciated that the coating is not necessarily, and in many cases is not, a layer applied to a previously formed substrate. Thus, articles in accordance with the invention may be made by a process in which heat-softened or molten material for forming the substrate is introduced into a mould before, after, or substantially simultaneously with, introduction of the softened or molten thermoplastic material for forming the coating. In the case of coextrusion processes, the coating and substrate are formed at substantially the same time using one or more dies rather than a mould. The coating may be on one or more surfaces of the substrate.

For the purposes of this specification, the coating is the outermost layer on the substrate. Thus, if there is an additional layer between the coating and the bulk of the substrate, that additional layer is regarded for the purposes of this specification as part of the substrate. Such an additional layer, which may readily

be produced using, for example, a multiple barrel injection moulding machine or by coextrusion followed by blow moulding, may, for example, be a polymeric paint layer with a metallic appearance on which the coating layer forms a clear coating, or a polymeric primer layer for a coating layer which is a paint layer. There may, however, be circumstances where it is advantageous for the coating layer to be in direct contact with the bulk substrate material, without the intervention of an additional layer between the two.

Where a moulding method is used for producing the article, the thermoplastic coating material is preferably (unless it forms part of a hollow article to be blow moulded) in molten or in a flowable softened form when it is applied to the mould or substrate surface, that is, the coating layer is preferably built up on the mould or substrate surface from a stream of molten or softened thermoplastic material, which may be in particulate form. Preferably, the coating is not, or does not form part of, a previously produced sheet of material which is subsequently brought into contact with the substrate or the substrate material.

As indicated above, the applicants have surprisingly found that the coating layer which forms part of polymeric articles in accordance with the invention may in many cases be suitable for use without additional treatment. Thus, for example, no curing step is necessary after moulding, and the appearance and properties of the coating may be such that it is not necessary to apply a further layer, for example, a paint layer or other protective layer, to the articles before use. Thus, for example, as indicated above, the coating may form a "paint" layer having desired properties and appearance. For such purpose, the coating advantageously has a thickness of at most 500 μm , preferably less than 200 μm , and in some cases coatings having a thickness of

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less than 100 μm are preferred, and coatings with these thicknesses may also be advantageous for other purposes, for example, when the coating is to provide an EMI shielding layer. Advantageously, coatings in accordance with the invention have a thickness of at least 5 μm . When a coating is said to have a particular maximum thickness, local areas of the coating may in some cases have a thickness greater than that maximum, although in other cases substantially the whole of the coating will not exceed the specified maximum. In general, thinner paint films will require proportionally more additives such as pigments to give the desired hiding power. In some circumstances, it is advantageous for the weight ratio of the substrate material to the coating material to be substantially greater than 1:1, for example, at least 2:1.

Desired properties may be imparted to the coating by, for example, the choice of appropriate pigments and/or other finely divided relatively infusible materials, for example, metallic materials, pearlescent materials and fillers, and appropriate levels of such materials, and/or by the inclusion in the coating of one or more additional substances, for example, UV stabilizers, thermal stabilizers, flow aids, pigment dispersing agents, impact modifiers, compatibilizers, haze controlling agents, stress cracking reducers, and antioxidants. (As discussed in greater detail later in the specification, the properties of the coating can also be modified by the choice of appropriate thermoplastic polymeric materials.)

By a finely divided relatively infusible material is meant a finely divided material which is substantially infusible at the temperature at which the coating material is applied and used, so that the finely divided material remains in particulate form in the polymeric material used for the coating and does not, for example,

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dissolve in that material. In many cases the finely divided relatively infusible material will be inorganic, but it may be organic, especially in the case of pigments. Advantageously, the finely divided material consists of or comprises one or more substances selected from pigments, metallic materials and pearlescent materials. A mixture of one or more different finely divided relatively infusible materials may be used. A substance which acts as a pigment may also, if appropriate, impart other desired properties to the coating. The finely divided substantially infusible material may if desired be electrically conductive, and, as discussed in more detail below, in some cases it may be desirable that the coating itself be electrically conductive. For the purposes of this invention a material is said to be finely divided if it does not interfere with the processing steps used in the manufacture of the article in accordance with the invention. The person skilled in the art will be familiar with particle sizes appropriate for infusible materials to be included in paint compositions.

Suitable pigments for inclusion in the coating layer of an article in accordance with the invention include, for example, ferric oxide, titanium dioxide, zinc oxide, quinacridones, phthalocyanines, for example, copper phthalocyanine complexes, anthraquinoids, thioindigo pigments, and carbon black. Pigments are advantageously used in a proportion of 0.5 to 35 wt %, based on the weight of the coating material. The proportion of pigment to be used in a particular case will depend on the colour of the pigment, and can be determined by routine experiment.

In some cases a desired colour may be imparted to a thermoplastic paint layer by a dye which is soluble in the thermoplastic layer rather than by the use of a pigment which remains in particulate form in the coating.

Such a dye may be used, for example, where a tinted transparent layer is required, although a dye may also be used where, for example, a finely divided substantially infusible filler material imparts opacity to the layer.

Finely divided metallic materials for inclusion in the coating layer include finely divided metals, finely divided metal derivatives, and metal-coated particulate materials. The metallic material may impart a metallic finish to the article. The metallic material may be in any suitable form, for example, in the form of particles, flakes, platelets, or fibres which may, if desired, be coated with an organic substance to aid dispersion in the thermoplastic material. Examples of suitable metals for use in coating compositions are nickel, aluminium, stainless steel and silver, and alloys containing one or more of these metallic materials. Examples of metal derivatives for use as the finely divided relatively infusible material are oxides, carbonyl compounds or salts. Materials in which a metal coating is applied to a particulate material include, for example, nickel-coated graphite and silver-coated graphite. As discussed in greater detail below, by suitable selection of the method for making articles containing finely divided metallic materials these materials can be forced either to the outer surface or to the inner surface of the coating layer. Metallic materials, if used, are advantageously present in a proportion of 5 to 25 wt %, preferably 10 to 20 wt %, based on the weight on the coating material.

Where the finely divided relatively infusible material is electrically conductive it may, if desired, be used in such a proportion and/or in such a manner as to impart antistatic, semiconductive, or electrically conductive properties to the coating. An electrically conductive material for use in this way may be, but is not necessarily, metallic. Thus, for example, carbon

black may be used to provide an antistatic coating, while finely divided silver may be used to provide a semiconductive coating. An electrically conductive coating may be particularly advantageous where EMI shielding of electrical components is desirable. Stainless steel fibres (for example fibres having a diameter of up to 300 μm and a length of up to 3 mm) are particularly advantageous for giving a coating layer capable of providing EMI shielding, although other metals, for example, nickel or aluminium may be used. A polymeric article in accordance with the invention in which the coating forms an EMI shielding layer may be used, for example, as an inexpensive, lightweight, housing for electrical equipment requiring shielding.

It is an advantage of the invention that aluminium can be used to give EMI shielding properties. Aluminium gives results greatly superior to those obtainable using nickel, but can only be used if it is protected from oxidation. As described in greater detail elsewhere in this specification, the present invention makes it possible to obtain articles in which aluminium in the coating layer is protected by a layer of polymeric coating material.

A coating composition comprising a finely divided metallic material may be used in accordance with the present invention to give a metallic finish on, for example, car body parts, without the need for further painting. Both aesthetic appeal and improved durability may be imparted by such a metallic finish. It may also be possible to give a metallic finish to transparent materials, for example, sunglasses or windows, by using a fine dispersion of metal particles in a colourless or tinted clear coating composition.

Pearlescent pigments include, for example, micaceous or ultrafine titanium dioxide, bismuth oxychloride; bismuth oxychloride or mica coated with

titanium dioxide; an iron oxide; and chromium oxide or hydroxide. Pearlescent materials, that is, materials which can impart a pearlescent effect to coatings containing them, may, if desired, be used together with finely divided metallic materials to enhance the decorative effect provided by the metals. Some pearlescent materials, for example, mica coated with titanium dioxide, also give a "sparkle" appearance. When pearlescent materials are used, they are advantageously present in a proportion of 5 to 25 wt %, preferably 10 to 20 wt %, based on the weight of the coating material.

UV stabilizers include, for example, hindered amines.

The coating properties indicated below are especially advantageous when the article in accordance with the invention is to be used as a vehicle component, but may also be advantageous in other circumstances.

The coating advantageously contains a UV stabilizer and, preferably, a pigment, in such a proportion that, after exposure for 200 hours in a QUV test as described below, the gloss of the coating, measured in accordance with ASTM D523-67, does not decrease by more than 50 % from the original level, and the coating shows no cracking, chalking or crazing.

In the QUV test, the coated article, or a flat portion thereof, is exposed in a QUV accelerated weathering tester fitted with 8 QUV 313nm-B lamps for 200 hours using the following cycle:

4 hours light with a black panel temperature of 60°C

4 hours dark with a black panel temperature of 50°C.

Condensation forms on the article during exposure. Periodically throughout the test the gloss is measured in accordance with ASTM D523-67, and a visual inspection is carried out.

Preferably, the coating has an abrasion resistance such that it passes a Taber test as specified in ASTM D1044, carried out using 250 cycles. The abrasion resistance can be varied, if desired, by choosing different fillers, polymeric materials and/or pigments, and/or different proportions of such materials.

Where impact resistance of the coated article is required, the impact resistance is preferably not more than 10 % less than that of the substrate material, and may be at least 2J measured as specified in BS 3900, 1973, Part E3. The coated article preferably exhibits ductile rather than brittle failure. Impact performance may be enhanced by the use of, for example, a thermoplastic (melt-processable) elastomeric material, for example a material as described later in this specification.

Preferably, the coating has a class A automotive finish comparable to that obtainable using a solvent-based paint. There should be no evidence of an orange peel effect. In accordance with the invention, a good finish can be obtained because the article can be made by a method in which the coating material is applied to a mould surface, which can be highly polished, in softened or molten form, especially good results being obtained when the coating material is applied in molten form.

Advantageously, the coating material has a softening point of at least 155°C, measured by the Vicat softening method (ISO 306 Method A), for a coating on polypropylene. Advantageous coatings may be obtained by using thermoplastic polymeric coating materials which begin to soften at a relatively high temperature.

The applicants have found that the invention makes it possible to produce articles which pass, for example, Rover Engineering Standard RES.30.EE.102 (June 1990).

In general terms, the present invention makes it possible to obtain high quality finishes, for example,

high quality paint finishes, which are superior to those obtainable by previously proposed methods using solvent-free coating materials. In some cases, a highly polished mould surface may be desirable to produce a surface with high gloss, and it may also be desirable to heat the mould surface. If a matt appearance is required, a grained mould surface can be used, and it may be desirable to maintain the mould surface at a relatively low temperature.

The article in accordance with the invention comprises a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof. The substrate and coating are substantially thermoplastic in the sense that each has a continuous phase or matrix of one or more thermoplastic materials. If desired, the entire coating or substrate may consist of thermoplastic polymeric material, but in most cases either the coating or the substrate or both will comprise one or more additional materials within the continuous phase provided by the thermoplastic polymeric material. Thus, for example, the thermoplastic continuous phase of the coating may have one or more finely divided materials uniformly or non-uniformly dispersed therein, and/or the thermoplastic continuous phase of the substrate may contain a reinforcing material, which could be in the form of a preformed reinforcing body, for example, a mat or bundle of elongate fibres or which could be dispersed homogeneously throughout the substrate. Alternatively, or in addition, the substantially thermoplastic continuous phase of the substrate may contain material present as a result of recycling thermoplastic articles containing finely divided relatively infusible material.

The article is preferably such that it is melt-processable, to permit, for example, recycling. In this case, any additional materials included in the article

as, for example, reinforcing materials or intermediate layers, should be such that they do not interfere with the melt-processing steps. Where it is desirable that the article be recyclable, the article preferably does not contain any intermediate layers, for example, bonding layers, which are infusible at the temperature at which melt-processing is carried out. The fact that the articles can be such as to be recyclable as a whole is a particular advantage of the invention.

As indicated above, the substrate and coating are substantially thermoplastic in the sense that each has a continuous phase or matrix of one or more thermoplastic materials. Articles in which the continuous phase is a thermosetting polymer would not have all the advantages obtainable in accordance with the invention. Thus, for example, such articles would not be melt-processable and thus could not readily be recycled. On the other hand, ionomeric materials, in which crosslinks in the form of ionic bonds between polymer chains are broken by heating of the material, but reform when the material is cooled again, can be melt-processed, and are thus included within the term "thermoplastic material" used in this specification, as are thermoplastic elastomers in which crosslinks are reversibly broken down on heating.

The possibility of using for the coating ionomers or thermoplastic elastomers or, in general, materials in which crosslinks are reversibly broken on heating, is a particular advantage of the invention, making it possible to obtain coatings, for example, thermoplastic paint coatings, with properties superior to those of thermoplastic coatings in which the thermoplastic materials do not contain crosslinks between chains at ambient temperatures. Reversibly crosslinkable materials are further discussed later in this specification.

Advantageously, the coating in the article of the invention comprises a thermoplastic polymeric material

which is compatible with the thermoplastic substrate material at least at the temperature at which the article is shaped in the mould. Compatibility of the coating and substrate materials enhances adhesion of the coating to the substrate, and is particularly desirable when the coating does not completely envelop the substrate.

Compatible polymers for use in accordance with the invention are preferably at least partly miscible at least at the temperature at which the article is shaped in the mould. With some coating/substrate combinations, however, it may be possible, particularly when using a thermal spraying step or dual injection step when making the article, to achieve some intimate mixing at the interface of the two materials which with controlled cooling may lead to coating material being trapped in the substrate material thereby giving an interpenetrating polymer network. (Such intimate mixing does not normally result when applying a coating material using electrostatic spraying techniques.) For the purposes of the invention, materials mixed in such a way are also regarded as compatible.

The use of thermal spraying and, in particular, flame spraying to apply a coating material may also make it possible to use initially incompatible coating materials which are rendered more compatible by the heat of the spraying system to give a bonded coating.

Adhesion can be improved (that is, compatibility can be enhanced) by the addition of compatibilizing agents to initially incompatible coating materials. Suitable compatibilizing agents include polymers having portions with an affinity to each of the polymers to be blended, and agents which produce a low level of crosslinking between the polymers without affecting the thermoplastic nature of the polymers.

In order to obtain good adhesion, it may be desirable for the coating material to comprise a polymer

in which the majority of repeating units are the same as the majority of repeating units in the substrate material, but this is not always essential.

The coating and substrate materials, and conditions of manufacture, are preferably chosen such that the article passes the crosshatch test (BS 3900 E 6/ISO 2409), which measures the adhesion of a coating to a substrate.

If the coating is completely to surround and encapsulate the substrate material then it is not always necessary for there to be good adhesion between the two. In such a case incompatible materials may be used without any modification. An incompatible coating encapsulating a substrate could be used to protect the surface of the substrate, the coating, which is not strongly adhered to the substrate, being readily removable to reveal a clean surface.

In some cases, the thermoplastic polymeric material used in producing the coating is chosen solely with a view to obtaining maximum adhesion to the substrate material. In other cases, however, the contribution that the thermoplastic polymeric material makes to the physical properties of the coating will also be of importance. The properties of the coating can be influenced by, for example, molecular weight of the polymeric coating material, the choice of particular types of polymeric coating materials, and/or the use of mixtures of polymeric coating materials.

A polymer with a higher molecular weight than that of the substrate may be preferred for the coating when it is desirable to produce a coating which is tougher and more durable than the substrate surface. It is an advantage of the present invention that the thermoplastic polymer used for the coating material may have a molecular weight higher than that normally usable when applying solvent-based paints and/or when applying

coatings electrostatically. Thus, for example, when applying a powdered coating material using electrostatic methods, the molecular weight and the melt flow index of the polymeric material are limited by the flow characteristics required to give a coating with an acceptable appearance. Articles of the invention are preferably made by a method in which the coating material is in a plastic condition when it contacts a mould surface, so that higher molecular weights can be tolerated. The use of polymers of higher molecular weight may make it possible to obtain coatings with superior scratch resistance, hardness and mechanical properties compared with coatings which are applied electrostatically to the mould surface.

In a preferred embodiment of the invention, the thermoplastic coating material comprises a reversibly crosslinkable thermoplastic polymeric material, for example, an ionomer or a thermoplastic elastomer, in which crosslinks are reversibly broken on heating. Where ionomers or thermoplastic elastomers are included in the coating material, the coating material preferably also comprises a further thermoplastic polymeric material, advantageously in a major proportion.

An ionomer is a thermoplastic material provided with a low degree of crosslinking in the solid state by the addition of a metal salt which provides ionic bonds between the polymer chains. The ionic links formed are thermally reversible and so melt processing techniques suitable for typical thermoplastic materials may be used to form products from the ionomers. Ionomers may if desired be blended with other types of polymers, for example, thermoplastic polymers mentioned in this specification. Where ionomer(s) is or are used, they advantageously form 5 % to 80 % by weight of the coating composition, preferably 5 to 15 wt %, especially about 10 wt %.

The ionic crosslinks in ionomers enhance the toughness/stiffness, the hardness, and the heat deflection temperature of coatings produced from coating materials containing the ionomers. Further, because free radicals (which could undergo unwanted reactions) are not formed when ionic links are broken, the impact resistance of the coatings is enhanced. Ionomers can also act to increase the compatibility of pigments with the polymeric material in the coating, and to enhance the paintability of the final coating. The properties of the final coating can be modified by appropriate choice of the proportion of ionomer in a thermoplastic polymer/ionomer blend used for the coating material and/or by appropriate choice of the level of crosslinking in the ionomer: the level of crosslinking will normally be dependent on the proportion of metal salt used in making the ionomer. Where a matt finish is required in the final product it may be desirable to use a relatively large proportion of ionomer: smaller proportions of ionomer may be desirable when a glossier finish is required.

The inclusion in the thermoplastic coating material of a reversibly crosslinkable melt-processable elastomeric material may be desirable to impart a desired impact strength to the coating. Such an elastomeric material, if present, preferably comprises from 1 to 70 % of the weight of the coating composition, amounts of up to 10 wt. % being preferred. An example of such a thermoplastic elastomeric material is a styrene-ethylene/butylene-styrene copolymer, which is crosslinked at ambient temperatures. The crosslinks are reversibly broken on the application of heat, thus allowing melt-processing of the material.

In a further advantageous embodiment of the invention, the thermoplastic coating material comprises a thermoplastic polymeric alloy. A thermoplastic alloy

may be obtained by melt-blending two or more thermoplastic polymers in the presence of a compatibilizing agent, the resulting alloy having chemical and/or physical properties superior to those of either of the individual polymers alone and to a simple mixture of the polymers. If desired, the compatibilizing agent may be added after the melt-blending step. An example of a thermoplastic alloy suitable for use in accordance with the invention is a polyamide/polypropylene alloy.

As indicated above, the coating material may comprise more than one thermoplastic polymeric material in order to impart desired properties to the coating. Thus, for example, the coating material may comprise a blend of a thermoplastic polymeric material having a good compatibility with the substrate material, and a second thermoplastic polymeric material which enhances the physical properties of the coating (and which may or may not also have good compatibility with the substrate). A number of advantageous blends are mentioned in this specification.

In one advantageous embodiment of the invention, the coating material comprises the main polymer component of the substrate material with the addition, where appropriate, of one or more substances selected from finely divided relatively infusible materials and the additional substances mentioned above as being suitable for imparting desired properties to the coatings. For example, polypropylene paints give very good coatings on polypropylene substrates. The polymeric material, for example, the polypropylene, of the coating may have the same average molecular weight as that of the substrate, or may, if desired, have a different, for example, higher, average molecular weight. One advantageous form of polypropylene for the coating material of the invention is linear polypropylene having a number average

molecular weight of more than 150,000 (measured by gel permeation chromatography) : an article containing this coating material is advantageously formed by dual injection. Particularly advantageous coating materials comprise a reversibly crosslinkable thermoplastic material as well as polypropylene.

In a further advantageous embodiment of the invention, the coating material comprises a blend comprising at least one polymer compatible with the substrate material and/or at least one polymer in which the majority of the repeating units are the same as the majority of repeating units in the substrate material, and at least one polymeric material, for example, a reversibly crosslinkable material, which imparts to the coating properties different from those of the substrate. Such a blend can be tailored to provide the properties required of the coating by varying the components and proportions of the blend. Thus, for example, an advantageous blend for use with a polypropylene substrate is a blend comprising a minor proportion of polyethylene, and, if desired, a reversibly crosslinkable material, and a major proportion of polypropylene, while an advantageous blend for use with a polyamide substrate is a polyamide/ polypropylene blend, for example, the polyamide/ polypropylene alloy sold by AtoChem under the trade name Orgalloy R60ES.

Examples of thermoplastic materials which may be used for the coating in an article of the invention include homo- and copolymers of propylene, and thermoplastic alloys containing propylene homo- and/or copolymers (for example, polypropylene/polyamide alloys), homo- and copolymers of ethylene, polyamides, ABS polymers, polystyrene, poly(meth)acrylates, polycarbonates, thermoplastic polyimides, polyesters, polyurethanes, polyvinylidene fluoride, and polyvinyl chloride. Blends and alloys of two or more of those

materials may of course be used.

The thermoplastic polymeric coating material is preferably chosen to minimize haze in the final coating layer.

Although the coating layer in the articles of the invention can be a paint layer which renders unnecessary the subsequent painting of the article, there may be circumstances in which the application of a further layer, for example, a clearcoat layer, may be desirable. Further, it may be desirable that a coating layer in the form of a paint be such that the paint can be touched up if the coating layer is damaged in use. For these purposes, it may be desirable to include in the coating layer a polymer, for example, a functionalized polyolefin, containing a relatively low proportion of polar groups, for example, carboxyl groups, or to include another additive which enhances the adhesion of a subsequently applied paint to the coating. It is however normally important that the proportion of polar groups should not be so high that the coating material readily sticks to metal: coating materials that readily stick to metals will not normally be suitable for use in in-mould coating methods. An appropriate level of polar groups can readily be determined by routine experiment.

Examples of coating materials suitable for use in accordance with the present invention are given in the copending application (No.) entitled "Coating Compositions" filed by Laporte plc on the same day as the present application.

A coating material for use in making the article of the invention may be prepared in any suitable manner. In one advantageous process, the thermoplastic polymeric matrix or carrier material is premixed, for example, in a tumble, fountain, or other mixer, with the desired additives, for example, a pigment, filler, metallic particles or UV absorber, and the mixture is melt-mixed,

cooled, and converted to particulate form. Melt-mixing, which facilitates thorough dispersal of the additives in the matrix material, may be effected using, for example, an extruder or a two roll mill. The molten mixture may then, for example, be passed through a die head and quenched at the die face or in a water bath to produce strands which are then pelletized by cutting blades. In one case, paint particles having a length of 3 mm and diameter of 2 mm were found to be advantageous when forming the article using a dual injection machine, although any size of particles suitable for the feed system of the injection moulding machine may be used.

In a further possibility certain of the additives, for example, metallic particles and/or pearlescent particles, are not added in the premixing step but are added at a later stage to prevent damage to the particles on processing. One means of achieving this is first to soften in a heated fluid bed dryer granules comprising all the components of the coating material apart from the metallic or pearlescent materials, and then to add the metallic or pearlescent particles, which stick to the exterior of the softened granules. Alternatively, a concentrate of the metallic or pearlescent particles in a compatible carrier can be introduced into the remainder of the coating material towards the end of an extrusion barrel.

When preparing coating materials for use in certain methods of manufacturing the articles of the invention (for example, flame spray methods), it may be advantageous to grind the material cryogenically to form a coating powder. Typically, when the coating material contains more than one component, the components are blended, the blend is extruded and formed into, for example, granules or pellets which are then cryogenically ground, the temperature in the mill being -50°C or lower, typically lower than -80°C . Other methods of preparing

thermoplastic powders may be used.

If desired, pigments and other substances to be incorporated in the coating layer may be blended with a relatively small proportion of the thermoplastic polymeric material to form a masterbatch, which may be blended, when desired, with the remaining thermoplastic material for forming the coating. The preparation of a masterbatch aids dispersion and makes it possible to avoid the use of powdered pigment in large scale manufacture. This is particularly advantageous for preventing pollution of the local environment and/or preventing the build up of potentially explosive dust mixtures.

In principle, any thermoplastic material can be used for producing the substrate in articles in accordance with the invention, although particular materials may have advantages in certain applications because, for example, of the physical properties and/or the cost of those materials. It is a particular advantage of the invention that the substrate material can be chosen without regard to the surface properties and/or the appearance of the article, which in many cases will make it possible to use low-cost and/or recycled material, for example, material containing mixtures of polymeric materials and/or containing pigments and/or other particulate substances derived from the melt-processing of recycled thermoplastics articles. Indeed, the recycled material can contain relatively large contaminants provided that these do not interfere with the processes used in making the articles or the properties of the articles. The substrate material may contain substances, for example, fillers, to impart desired properties to the materials and may, if desired, contain a blowing agent so that a foamed substrate is obtained.

Examples of suitable substrate materials are homo- and copolymers of propylene, homo- and copolymers of ethylene, polyamides, ABS polymers, polystyrene, poly(meth)acrylates, polycarbonates, thermoplastic polyimides, polyesters, polyurethanes, and polyvinyl chloride, and blends and/or alloys of those polymers.

As indicated above, the article of the invention may be made by any suitable method. Preferred methods for forming the article involve shaping the coating and the substrate in the same mould after sequential or simultaneous introduction of the coating material and substrate material into the mould, although coextrusion methods can be used where it is appropriate to do so.

Examples of methods by which the coating material can be introduced into a mould are thermal spraying, particularly flame spraying, in which coating material is sprayed onto a surface of the mould under conditions such that it is in a softened or molten condition before it contacts the surface; injection of molten coating material into the mould and thus onto the mould surface; and application of the coating material to the mould surface in powder form, for example, by electrostatic spraying, and then melting the powder to form the coating. Methods in which the coating material is in a softened or molten form (including a mixture of softened and molten material) before it contacts the mould surface are preferred.

In some cases, it may be advantageous to apply the coating material to the substrate material rather than to a surface of the mould. Thus, for example, the coating material may be sprayed onto the substrate material, for example, by thermal spraying, following which the substrate material is positioned in the mould. Alternatively, the coating material may be applied to a support to form a coating layer which is then stripped off the support and positioned in the mould.

The substrate material may be introduced into the mould in any suitable manner. Thus, for example, the substrate material may be in the form of a coherent mass which is positioned as such in the mould and then submitted to a compression moulding step. In this case the coating material can be applied to a surface of the substrate material, preferably before the substrate material is positioned in the mould, or to a surface of the mould.

In another advantageous method, the substrate material is injected into the mould in molten form. In this case, the coating material is advantageously either applied to the mould by thermal spraying, before injection of the substrate material into the mould, or is injected before, simultaneously with, or after injection of the substrate material. If desired, the substrate material can be introduced into the mould in the form of foamed or foamable material.

In another method for forming articles according to the invention, the coating material and substrate material are simultaneously extruded through an extrusion die in a coextrusion step. If desired, the extruded article may be subjected to a blow-moulding step. An article formed by dual injection may also, if desired, be subjected to a blow-moulding step.

Because articles according to the invention comprise a thermoplastic coating material and a thermoplastic substrate material, no curing of the coating or substrate is necessary after moulding. The finished article can simply be removed from the mould, if necessary after cooling of the article, or allowing it to cool. If desired the article can be cooled out of the mould.

Additional information about preferred processes for making the articles of the invention is given below.

As indicated above, one advantageous method for forming the coating involves spraying the coating

material onto a surface under conditions such that it is in a molten and/or softened condition before it contacts the surface. The coating material can then coalesce on the surface to form a substantially continuous coating layer. This method is very suitable for the production of injection moulded articles and compression moulded articles, and may if desired be used in the production of articles moulded by other methods.

The surface onto which the coating material is sprayed may be a surface of the mould, a surface of the substrate material, or a surface of a support from which the coating layer can be removed, in coherent form, and then positioned in the mould. Preferably substantially all the coating material is in softened or molten form (or is a mixture of softened material and molten material) before it contacts the surface, although a minor proportion may still be in solid, non-plastic form provided that it melts and flows on contact with the surface or the softened or molten coating material thereon. In the preferred case, where the coating material is molten before it contacts the surface, it does not depend on the heat of the surface to melt it, although additional heat may be supplied by either or both of the mould and the substrate material, if desired, or by the support. Thus, for example, it may be desirable to maintain the mould at a temperature above ambient temperature, but below the melting temperature of the substrate material, to achieve good cycle times and substrate and coating formation.

The coating material may be, for example, applied to a surface, for example, an interior surface, of an open mould or to a surface of a closed mould.

Heat may be applied to the coating material, before it contacts the surface, by any suitable external energy source. Thus, for example, a hot air gun may be used to heat the air through which a powdered coating material

passes as it travels towards the surface. Alternatively, detonation spraying or plasma spraying, in air, or in a vacuum chamber or high pressure chamber, may be used. Preferably, however, the coating material is applied to the surface using a flame spray gun. The coating material, in the form of a powder, may pass down the centre of a flame, or around a flame, and is heated by hot gas, for example, hot air. If the correct conditions, including temperature and particle size, are chosen then the powder is not burnt by the flame, but is heated enough to soften or melt it. The most appropriate particle size for any given powder can be determined by routine experiment. The most suitable range of particle sizes in any particular case is dependent on the gun setting used.

When the coating material is applied by thermal spraying, the material for forming the substrate may be introduced into the mould by any suitable method, for example, by injection of the substrate material at such a temperature that the substrate material is molten, or by the introduction of a self-supporting sheet or preform of substrate material, which may contain, for example, a reinforcing material, for example, glass fibres, and which may, if desired or required, be heated before introduction into the mould. (The use of a self-supporting sheet or preform of substrate material may be useful, for example, for producing floor or ceiling tiles.) In general, the coating material is applied to the mould surface before, or substantially simultaneously with, introduction of the substrate material into the mould. The coating material and substrate material may be shaped to produce an article in accordance with the invention by any desired moulding method, for example, injection moulding or compression moulding. Additional heat may be supplied, if necessary, during the moulding process. When moulding is complete, the moulded article

is, if necessary, cooled or allowed to cool, and is then removed from the mould.

The applicants have surprisingly found that, when using the above-described method, durable coatings can be obtained on plastics substrates, even when the substrate material is injected at high velocities. The application of coating material to mould surfaces by previously proposed methods, for example, electrostatic spraying, tends to lead to flow lines being formed in the powder when substrate material is injected at high velocity. Thermal spraying makes it possible to obtain uniform coating layers of a desired thickness. The coating thickness may be controlled by appropriate choice of spraying conditions.

As indicated earlier in this specification, the coating material may comprise one or more metallic materials in finely divided form, for example, as particles, fibres or flakes. It has been found that when particles of metallic materials are included in coating materials used in the above-described thermal spraying method to give coated injection moulded products, the particles are forced to the surface of the coating giving an excellent decorative finish. When the same coating material is used for producing compression moulded products it is found that the metal particles are forced towards the interface of the coating and substrate. This would be useful for EMI shielding of electrical components.

In a second aspect the present invention provides a method of manufacturing an article comprising a substrate having a coating on at least one surface thereof, wherein a polymeric coating material and a polymeric substrate material are introduced into a mould and are shaped in the mould to produce the article, if necessary with the application of heat, the coating being formed by spraying the coating material onto a surface under conditions such

that substantially all the coating material is in a softened or molten condition before it contacts the said surface. The surface onto which the coating is sprayed may be a surface of the mould, a surface of the substrate material, or a support surface from which the coating can be stripped and then positioned in the mould.

Spraying is preferably effected by flame spraying. Accordingly, the invention also provides a method of manufacturing an article comprising a substrate having a coating on at least one surface thereof, wherein a polymeric coating material and a polymeric substrate material are introduced into a mould and are shaped in the mould to produce the article, if necessary with the application of heat, the coating being formed by flame spraying the coating material onto a surface.

The method steps indicated above in connection with the manufacture of articles of the invention by thermal spraying may of course be used in the method that forms the second aspect of the invention. Preferred coating and substrate materials for use in the method, and preferred characteristics of the articles produced, are those discussed above in connection with the articles of the invention. The invention also provides articles, in particular vehicle components, produced by the thermal spraying method that forms the second aspect of the invention.

In accordance with the second aspect of the invention, the coating material, particularly a coating material used for coating a thermoplastic substrate, advantageously comprises a thermoplastic material, particularly a thermoplastic material which is compatible with the substrate material. (As indicated above, the term "thermoplastic material" includes reversibly crosslinkable materials in which bonds between polymer chains are broken by heating of the material, but reform when the material is cooled again.) In principle,

however, any material could be used for the coating in the second aspect of the invention provided that it can be applied in softened or, preferably, molten form and can remain formable during moulding of the substrate material. If a thermosetting material is used for the coating material or the substrate material, additional heat may in some cases be required to cure the material. In this aspect of the invention it is in principle also possible to use a thermosetting material for the substrate.

The thermal spraying method makes it possible to obtain high quality, durable coatings on, for example, thermoplastic substrates, for example, polypropylene or polyethylene substrates, which cannot be satisfactorily coated, at reasonable cost, by previously proposed methods. Good adhesion of the coating can be obtained without the need to modify the surface of the substrate by prior treatment (for example, flame treatments, corona discharge, chemical etching or plasma treatments) or by modification of the bulk polymer. The production of coated substrates may be achieved with short cycle times and, where coatings of low surface energies are used, without the use of release agents on the mould surface. Further, because the coating material is in softened or molten form when it comes into contact with the mould, any excess material is normally removed from the mould with the moulded article, so that little or no cleaning of the mould is necessary, even when the mould is to be used for articles of a different colour. The preferred embodiment of this method, wherein the coating material is applied using a flamespray gun, can be used in large production lines (where the gun can, for convenience, be mounted on a robotic arm) and in individual injection moulding or compression moulding machines for smaller-scale use.

In a further advantageous method of manufacturing an article according to the invention, a thermoplastic polymeric material for forming the coating is heated to a plastic condition and is injected into a mould, a thermoplastic polymeric material for forming the substrate is heated to a plastic condition and is injected into the mould, and the coating material and substrate material are shaped in the mould to produce the article.

In this method, referred to herein as a multiple-injection method, the coating material may be injected into the mould before, after, or at substantially the same time as, the substrate material. The coating material is preferably heated to a temperature above the softening range of the thermoplastic polymeric coating material before being injected into the mould.

In a preferred embodiment of the invention, the article is made by a multiple-injection method, the coating material being heated to a plastic condition in a chamber and injected into the mould through an aperture, and preferably through a channel, having an internal diameter smaller than the internal diameter of the chamber. This aspect of the invention will be described in greater detail below. The internal diameter of the aperture (or channel) is advantageously less than 75 %, preferably less than 50 %, of that of the chamber. Advantageously, the chamber is an extruder barrel through which the coating material is propelled, and the aperture is an injection port.

The coating material and substrate material are preferably injected into the mould using a multibarrel injection machine: although a single barrel machine could be used, that is less advantageous. In many cases a dual injection machine will be used, although a machine with more than two barrels will be appropriate when making an article having more than one layer on the bulk substrate

material. Thus, for example, it may be desirable to provide a primer layer and an outer layer adhering to the primer layer.

The multiple-injection method described above has, in common with the thermal spraying method described earlier, the advantage that the coating material does not depend on heat supplied by the mould to render it plastic, although additional heat may be supplied by either or both of the mould and the substrate material, if desired. Thus, it may be desirable to maintain the mould at a temperature above ambient temperature, but below the melting temperature of the substrate material, to achieve good cycle times and substrate and coating formation.

A further advantage of the multiple-injection method of forming the article, which it shares with methods in which the coating material is injected into the mould in molten form and the substrate is formed by a method other than injection moulding, is that the injection step tends to cause any finely divided relatively infusible materials in the coating material to be incorporated in the coating layer rather than floating to the outer surface thereof, which tends to occur when, for example, solvent-based paints are used. The relatively infusible materials, for example, metals, are thus protected from abrasion and weathering by a layer of polymeric material, thus obviating the need for a top coat, for example, a lacquer coating layer. Thus, for example, as discussed earlier, finely divided aluminium may be used in the coating layer without the need for a lacquer clear coat.

When the coating material comprises a finely divided relatively infusible material the particles of which have one or two dimensions substantially greater than the other two or one, the coating material is advantageously heated in a chamber and is injected into the mould through an aperture having an internal diameter less than

the internal diameter of the chamber, as discussed above. Such a coating material is advantageously injected at a pressure of at least 50, preferably at least 500, bar (5 and 50 MPa respectively). Preferably, the coating material passes from the chamber to the aperture via a channel having a diameter smaller than that of the chamber.

The applicants have surprisingly found that when a coating material containing a finely divided relatively infusible material the particles of which have one or two dimensions substantially greater than the other two or one is injected through a relatively narrow injection port, and especially when such a material is injected via a relatively narrow channel, the particles of relatively infusible material tend to become orientated in the coating layer, enhancing the appearance and/or performance of the coating.

Thus, in accordance with the invention, a heating chamber having an exit aperture of internal diameter or internal cross-section less than the internal diameter or internal cross-section of the chamber may be used to enhance the orientation of a finely divided relatively infusible material in a thermoplastic coating forming part of an article comprising a substrate having a substantially thermoplastic coating on at least one surface thereof, the coating material comprising a finely divided relatively infusible material the particles of which have one or two dimensions substantially greater than the other two or one.

When the substantially infusible material comprises metal particles and is injected through a relatively narrow aperture, and especially when such a material is injected through a relatively narrow channel, the applicants have found that the metal particles tend to be orientated in the coating layer, giving a highly reflective effect. Particularly advantageous results may

be obtained if the injection pressure is greater than 500 bar (50 MPa) and the aperture has an internal diameter less than 50 % of that of the heating chamber.

The applicants have also found that advantageous results are obtained, when injecting through a relatively narrow aperture, when the coating material contains a finely divided pearlescent material, or a finely divided pearlescent material and a finely divided metallic material, again because orientation of the finely divided material tends to occur.

Orientation of finely divided material is also of importance in coatings used to provide electromagnetic shielding, and the applicants have found that performances equivalent to those obtainable when applying a coating using a solvent-based coating system can be obtained.

In one advantageous method, a coating material containing stainless steel fibres 300 μm in diameter and 3 mm long was injected through a relatively narrow aperture and gave an attenuation of 55 to 65 dB across a range of 300 MHz to 1 GHz. In this method, the coating material was injected at a pressure of at least 1000 bar (100 MPa), and such pressures are preferred for producing coatings with electromagnetic shielding properties.

An orientation effect may also be obtained in a coextrusion process in which the die diameter is smaller than the barrel of an extruder feeding material to the die.

In one advantageous dual-injection method for forming an article according to the invention, particles of solid paint are fed into one or more feed hoppers of a multibarrel moulding machine. In the case of hygroscopic materials it may be necessary to feed via a dehumidifier or industrial dryer to prevent absorption of water. The paint system is passed into an extruder

barrel and conveyed to the end of the barrel using a screw suitable for the material. If, as is preferred in many circumstances, the additives are predispersed in the matrix material (for example, by a method as described above), further dispersal of the additives is not normally necessary at this stage, thus making it possible to use relatively low shear rates. The substrate material may be conveyed to the injection nozzle in a separate extruder barrel.

The injection of the coating and substrate materials in a multiple injection method may be controlled in any suitable way, but will typically be controlled by a computer-operated valve system. Some machines use a screw which conveys a wad of coating material or substrate material to an injection point and then acts as a plunger to force a controlled volume of material into the mould. In certain types of machine the coating material is injected slightly ahead of the substrate material so that the coating material is applied to the inner surface of the mould and the mould is then filled with substrate material. Other designs of nozzle allow the coating material and substrate material to enter the mould substantially simultaneously via concentric nozzles.

The thickness of coatings in articles made by the multiple-injection method may readily be controlled by appropriate choice of the injection conditions. The applicants have found that the multiple-injection method makes it possible to obtain thin coatings of excellent quality (for example, with coating thicknesses and properties as mentioned earlier in this specification) even when moulding articles of relatively complex shape. In some cases the coating thickness can be controlled such that one part of an article has a thicker coating than another: this is of advantage in articles, for example, vehicle wheel trims, where one part of the

article is subjected to greater wear in use than another. The multiple-injection process also has the advantages discussed elsewhere in this specification of in-mould coating processes using a coating material that is in a softened and/or molten form when it comes into contact with the mould surface.

A particular advantage of the multiple-injection method is that it makes it possible, especially where highly polished moulds are used, to obtain articles, for example, vehicle components, having a paint layer with a sufficiently high gloss for use without further treatment even in circumstances where a high gloss finish is essential. The method thus represents a major advance in, for example, the manufacture of vehicle components comprising thermoplastic substrate materials.

In a third aspect the present invention provides a method of manufacturing an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, wherein a polymeric material for forming the coating is heated to a plastic condition and is injected into a mould, a polymeric material for forming the substrate is heated to a plastic condition and is injected into the mould, and the coating material and substrate material are shaped in the mould to produce the article, if necessary with the application of heat, the coating material comprising (a) one or more substances selected from finely divided metallic materials, finely divided pearlescent materials, and UV stabilizers and the method being carried out such that the coating has a thickness of at most 500 μm , and/or (b) at least one thermoplastic reversibly crosslinkable polymeric material.

The method steps indicated above in connection with the manufacture of articles of the invention by a multiple-injection process may of course be used in the

method that forms the third aspect of the invention. Preferred method steps, preferred coating and substrate materials for use in the method, and preferred characteristics of the articles produced, are those discussed above in connection with the articles of the invention. The invention also provides articles, in particular vehicle components, produced by the multiple-injection method that forms the third aspect of the invention.

A further, advantageous method of manufacturing an article according to the invention uses blow moulding to shape a hollow article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof. The hollow article may be formed by a suitable method, for example, dual injection, but is preferably formed by coextrusion of the substrate material and the coating material through a common extrusion die. Suitable methods for forming the hollow article will be known to those skilled in the art. Blow moulding is particularly suitable for producing containers, bottles and fuel tanks with narrow entrances.

The thicknesses of the coating and substrate in blow moulded articles in accordance with the invention may be controlled by choice of appropriate layer thicknesses in the hollow article to be blow moulded (for example, by the choice of appropriate extrusion dies), and by suitable control of the blowing process. Suitable methods will be known to those skilled in the art.

In a fourth aspect, the invention provides a method of manufacturing an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, wherein a hollow article comprising a layer of substrate material and a layer of coating material is positioned in the mould and a fluid is introduced into the hollow

article to force the article into contact with the mould, heat being applied if necessary, the coating material comprising (a) one or more substances selected from pigments, finely divided metals, finely divided pearlescent materials, and UV stabilizers, and/or (b) at least one thermoplastic reversibly crosslinkable polymeric material and articles, particularly vehicle components, made by the method. Preferred coating and substrate materials for use in the method, and preferred characteristics of the articles produced, are those discussed above in connection with the articles of the invention.

Various advantages of the present invention have already been mentioned in this specification. It will be appreciated that the present invention makes it possible to form, for example, articles from a low-cost thermoplastic material, including recycled material, without the need to incorporate large quantities of additives into the material to impart desired properties or a desired appearance to the bulk of the material. Instead, any additional substances can be confined to the coating layer, and it is feasible to use for the coating layer, if desired, relatively expensive materials, for example, high performance engineering polymers, including polymer blends and alloys. The problems inherent in the use of solvent-based coating methods are also avoided. If desired, the coating can be chosen to be such that a further coating layer, for example, a clear lacquer coating, can be applied over it, although the invention will normally make it possible to dispense with such lacquer coatings. The coating material can be supplied as a solid, solventless, thermoplastic paint in, for example, granulated or powdered form, and does not require curing.

When a metal-containing coating material is used it may be necessary to coat the mould with a release agent

before applying the coating material. Other coating compositions used to give coatings may not require release agents to be used if, for example, the coating material has a low surface energy so that it has little tendency to adhere to the mould.

In particular the invention makes it possible to provide vehicle components which are formed from a thermoplastic substrate material and which have a high quality coating layer which can be obtained without the application of a sheet of coating material to a preformed substrate. The invention thus represents a major advance in the automobile industry, solving a problem (the manufacture of coated thermoplastic vehicle components) which has been the subject of extensive research in the industry.

A number of articles according to the invention, and methods for making such articles, will now be described, by way of example only, with reference to the accompanying drawings, in which:

Fig. 1 is a diagrammatic representation of one form of flame spray gun which may be used in making an article according to the invention;

Fig. 2 is a diagrammatic representation showing the application of a coating material to the mould of an injection moulding machine using another form of flame spray gun;

Fig. 3 is a diagrammatic representation showing the parts of the mould shown in Fig. 2 brought together, with substrate material injected into the mould;

Fig. 4 shows a vehicle component made using a moulding method of the type illustrated in Figs. 2 and 3 and includes an encircled enlargement of a section of the component;

Fig. 5 is a diagrammatic cross-section through another form of flame spraying apparatus;

Fig. 6 is a diagrammatic cross-section through one part of a two part mould with a coating layer of paint being applied thereto by flame spraying;

Fig. 7 is a diagrammatic cross-section showing the other part of the mould of Fig. 6 and three glass mat-filled polypropylene sheets arranged therein above the paint layer;

Fig. 8 is a diagrammatic cross-section through the mould of Fig. 7 showing the mould parts brought together to compress the sheets and bond the material of the sheets together and to the layer of paint;

Fig. 9 shows the mould parts separated and the component formed therein;

Fig. 10 shows diagrammatically a preform tool with a layer of paint being applied thereto by flame spraying;

Fig. 11 shows the layer of paint formed in Fig. 10 removed from the preformed tool for introduction into the mould;

Fig. 12 is a diagrammatic representation showing the application of a layer of paint to a substrate material;

Fig. 13 is a diagrammatic cross-section through a two part mould showing the coated substrate material of Fig. 12 positioned therein;

Fig. 14 is a diagrammatic cross-section through one form of dual injection machine which may be used for making an article in accordance with the invention;

Fig. 15 is a diagrammatic cross-section through part of another form of dual injection moulding machine showing the injection into a mould of a granulated plastics paint material in a plastic condition;

Fig. 16 shows the introduction of a substrate material into the mould of Fig. 15;

Fig. 17 shows the machine of Fig. 15 after injection of the substrate material is complete;

Fig. 18 shows a second injection of granulated plastics paint material in a plastic condition to finish

the moulding step;

Fig. 19 is a cross-section to a larger scale through part of an article made by injection moulding;

Fig. 20 is a cross-section to a larger scale of an article which comprises a paint having metallic effect additives;

Fig. 21 is a perspective view of a vehicle wing in accordance with the present invention and includes an encircled enlargement of a section of the wing;

Fig. 22 is a cross-section of part of the wing of Fig. 21 on the line XXII - XXII in Fig. 21;

Fig. 23 is a diagrammatic cross-section through part of an extruded hollow article;

Fig. 24 is a diagrammatic view of the hollow article positioned between separated mould halves of a blow moulding tool;

Fig. 25 is a cross-section through part of the blow moulding tool shown in Fig. 24 with the mould halves brought together and with the hollow article inflated within the mould;

Fig. 26 is a cross-section to a larger scale through the moulded article formed in Fig. 25 removed from the mould;

Fig. 27 is a perspective view of part of the rear end of a vehicle showing a spoiler in position thereon;

Fig. 28 is a transverse section through part of the spoiler shown in Fig. 27;

Fig. 29 is a diagrammatic elevation of part of a blow moulding machine suitable for producing the spoiler shown in Figs. 27 and 28 and illustrates an extruded hollow article in position between mould halves, the mould halves being shown in cross-section;

Fig. 30 shows the mould halves of Fig. 29 closed and the extruded hollow article inflated so as to conform to the mould;

Fig. 31 is a view to a larger scale of part of the mould in Fig. 30 showing part of the inflated hollow article;

Fig. 32 shows the mould halves separated to enable the completed spoiler to be removed;

Fig. 33 is a view similar to Fig. 31 but showing a moulded article having three layers of material;

Fig. 34 is a diagrammatic cross-section of part of an extruded article drawn to a larger scale and showing flake-like additives in its paint layer;

Fig. 35 is a perspective view of part of an article in accordance with the invention in the form of a vehicle bumper;

Fig. 36 is a cross-section on a larger scale through part of the bumper shown in Fig. 35; and

Fig. 37 shows an article in accordance with the invention in the form of a wheel trim.

Referring to the drawings, Fig. 1 is a diagrammatic representation, not to scale, of one form of flame spray gun which may be used in making an article according to the present invention.

A material to be sprayed, a coating composition 1, is supplied in powder form to a container 2. Compressed air is blown into the powder container through a conduit 3, forcing a powder/air mixture to flow out through a pipe 4 into a torch 5. Fuel gases are supplied to the torch via pipes 6 and 7, oxygen being supplied via pipe 6 and acetylene being supplied via pipe 7. The rate of supply of the fuel gases can be controlled as can the rate of supply of the compressed air, and thereby the supply rate of the powder. The fuel gases travel down the centre of the torch, through pipe 8, and are ignited at the torch tip 9 to form a flame. The powder/air mixture flows down a channel 10 in the torch and is focussed into a concentrated jet at the tip of the torch. The heat of the flame heats the particles causing them to

soften or melt and the hot expanding fuel gases/product gases propel them towards the surface to be coated.

Figs. 2 to 4 show the use of a flame spraying apparatus in the production of a component for the interior of a vehicle, and a vehicle component produced by a method as described with reference to Figs. 2 and 3.

Fig. 2 shows an injection mould 20 comprising mould halves 21 and 22, the mould half 22 being associated with an injection barrel 23 provided with a screw 24. The interior of the barrel 23 communicates with the interior of the mould via a conduit 25.

In Fig. 2, a flame spray gun shown diagrammatically at 26 is positioned so that coating material can be applied to the interior surface of the mould half 21, a coating 27 having previously been applied to the interior of the mould half 22 using the flame spray gun 26.

Fig. 3 shows the mould closed, with a continuous coating 28 on its inner surface. In Fig. 3, substrate material 29 has been injected from the barrel 23 to fill the mould.

Fig. 4 shows a vehicle component 30, in this case a battery tray, formed by a method of the type described with reference to Figs. 2 and 3. The component includes a coating layer 31 formed by flame spraying the surfaces of an appropriate mould and a core 32 formed by injection moulding.

Another form of flame spraying apparatus is shown in Fig. 5. In Fig. 5, flame spraying apparatus 101 comprises a nozzle 102, a container 103 for powdered plastics paint 104 which is fed to the nozzle 102 by a feed device 105, an acetylene gas supply 106 and a compressed air supply 107. The acetylene and compressed air are fed to the nozzle 102 and ignited at the outlet end 108 of the nozzle. Particles of the powdered plastics paint 104 are fed to the nozzle and are brought to a softened-flowable condition in the flame. In that

condition, the ignited gas and air project them as globules 109 towards a target. On striking the target, the globules coalesce to form a layer.

In Fig. 6, flame spraying apparatus 101 sprays globules of powdered plastics paint onto a surface 112a of a mould part 112, which forms part of a mould indicated generally as 110 (see Fig. 8). The mould part 112 has a temperature in the range of 60°C to 70°C. The sprayed paint then coalesces to form a uniform layer 116 on the mould surface 112a. One or more heated sheets 117 of plastics material, for example sheets of glass fibre-reinforced polypropylene, are then placed in the mould as shown in Fig. 7. An upper part 113 of the mould 110 is then urged downwardly so as to compress the sheets 117 and cause them to flow and spread outwardly over the surface of the paint layer 116 as in Fig. 8. The heated sheets (which may be, for example at a temperature in the range of from 160°C to 200°C) raise the temperature of the layer 116 to ensure that it is sufficiently plastic to bond to the material of the sheet or sheets 117. Once the moulded article has cooled sufficiently, it is removed from the mould 110 as in Fig. 9.

Instead of flame spraying the paint into the mould part 112, it can be sprayed into a preform tool 120 as shown in Fig. 10 having a cavity 122 which is substantially the same shape and size as a cavity 114 defined by the mould part 112 (see Fig. 11.) Once the sprayed paint layer 116a has cooled sufficiently, it is removed from the tool 120 as a preformed film of paint for placing in the mould part 112 as in Fig. 11. One or more plastics sheets 117 can then be introduced into the mould as described with reference to Figs. 7, 8 and 9.

When the coating material is sprayed against the mould surface 112a, the quality of the surface finish on the moulded article is dictated by the finish of mould surface 112a. Thus, a very smooth finish on surface 112a

will provide a glossy paint finish on the moulded article, when the coating material is a paint. The thickness t of the coating layer 116a may be in the range of, for example, 0.2 mm to 1.0 mm which will help to hide any surface irregularities of the substrate material 117, particularly where the latter comprises fibre-reinforced material.

Fig. 12 shows the flame spraying apparatus 101 being used to spray molten globules of a powdered plastics paint directly onto substrate material 130 to form a coating layer 131 thereon. In Fig. 13, the coated substrate material is shown positioned between the two halves 112 and 113 of a mould 110 as shown in Fig. 7 to 9. Moulding is completed by the steps illustrated in Figs. 8 and 9.

Fig. 14 shows a dual injection machine comprising two barrels, 201 and 202, each of which extends substantially horizontally. (It is also possible for the barrels of a dual injection machine to be arranged vertically.) Each of the barrels comprises a cylindrical body portion 203 having a hopper 204 mounted on the upper portion thereof. Each barrel includes a screw 205 for forcing material introduced via the hopper 204 towards an exit aperture 206 at one end of the barrel. Each exit aperture has a diameter less than that of the body portion of the respective barrel.

Each exit aperture 206 is connected to an injection nozzle 209 via a channel, the channel from the barrel 201 being indicated by the reference numeral 207 and that from the barrel 202 being indicated by the reference numeral 208. The channel 207 communicates with an annular nozzle portion 210 of the nozzle 209, which surrounds a nozzle portion 211 into which the channel 208 opens. The nozzle 209 is in communication with a cavity 212 in a mould 213 comprising two mould portions 214 and 215.

In use of the dual injection machine, thermoplastic coating material can be introduced into the barrel 201 and thermoplastic substrate material can be introduced into the barrel 202, the materials being rendered plastic by the action of the screws and, normally, the application of heat. The plastic material is forced through the respective apertures 206 to the nozzle 209, and then into the mould. Flow of the materials can be controlled by any suitable means (not shown) such that the desired article is produced.

In apparatus of the above type, either of the barrels can, if desired, be used independently of the other.

A further dual injection machine is shown diagrammatically in Figs. 15 to 18.

The injection moulding machine shown in Figs. 15 to 18, has a mould 310 having first and second halves 312, 313, defining a hollow cavity 314 therebetween. The hollow cavity 314 is in communication with a block 315 which contains a first passageway 316 for material from a first extruder 317 and a second passageway 318 for material from a second extruder 319. A rotary valve 320 is positioned between the block 315 and an inlet port 322 in the mould half 313, which inlet port communicates with the cavity 314 to allow selection of the material to be injected into the cavity 314.

The extruder 317 is associated with a heater 317a and is operated to deliver a coating material 323 formed by heating a granulated thermoplastic paint material 323a to a plastic condition.

As shown in Fig. 15, an initial quantity of the coating material 323 is injected into the cavity 314, the mould 310 being at a temperature in a range of, for example, 20°C to 100°C. The valve 320 is then rotated to shut off the feed of material 323. As shown in Fig. 16, a thermoplastics substrate material 324a is heated in a

heater 319a associated with the second extruder 319 and the heated substrate material is injected into the cavity 314 behind the injected material 323, as shown in Fig. 16. The injection of the material 324 causes it to spread the coating material 323 over the mould surfaces 314a defining cavity 314 and injection is continued until the surfaces are completely coated with the material 323 and the material 323 envelopes the material 324. The material 324 thus forms a thermoplastics substrate or core, as shown in Fig. 17, having a coating or skin formed by the material 323.

In Fig. 18, the valve 320 is rotated again to shut off the feed from the extruder 319 and to permit injection of the coating material 323 into the port 322 so that the machine is ready for another injection cycle and so that the core material is completely enveloped in coating material.

It is preferred to use a single gate (inlet port 322 in Figs. 15 to 18) on the machine and to position the gate to provide equal flow lengths within the mould. Weld lines on the finished article can be predicted and accommodated in styling lines of the article. Where a surface with high gloss is required, the mould surfaces are preferably highly polished to provide the desired finish, and may be chromium plated. Good venting of air from the mould is also important.

The depth d (Fig. 19) of the coating material can be selected to be at least as thick as a paint coating which would normally be applied to, say, a car body component by paint spraying or dipping. Also, the mould 310 can provide a superfine surface finish for the coating which will compare well with that obtained by spray or dip painting. Moreover, by producing a coating in a dual injection moulding process, the finished coating will be free from contamination by air-borne dust as well as being uniform and consistent. Also, the

method is cleaner and more environmentally friendly than producing a finish using a conventional paint facility as the process does not involve extracting contaminated air or effluent from a paint shop into the atmosphere.

The substrate material 324 may if desired be injected as a foamed or foamable thermoplastic material.

Fig. 20 shows paint layers having a metallic effect. The granulated plastics paint coating material 323a includes metallic and/or pearlescent flakes 340. The flakes 340 provide a metallic and/or pearlescent finish in the paint coating. It has been found that the injection process causes the flakes 340 to orientate themselves so that they lie generally in a plane parallel with the flow or spread direction indicated by arrow F and generally parallel with the plane of the coating formed by the coating material 323. Also the flakes 340 are constrained to lie within the confines defined by the surfaces 314a of the cavity 314 so that they do not project from the finished paint surfaces of the moulded article. In fact, the flakes will normally lie sufficiently far below the exposed surface of the coating material to be protected against, for example, oxidation, thus making it possible to use materials, for example aluminium, which would be adversely affected by oxidation.

The dual injection method can be used to produce, for example, various body components of a motor vehicle having a paint finish provided by the coating material. An example of a vehicle body wing which may be produced by dual injection is shown in Figures 21 and 22.

A mould normally used for the injection moulding of a vehicle front wing for subsequent spray or dip painting after removal from the mould was positioned on a machine for providing dual injection of plastics material. The two extruders of the machine were supplied with coating and substrate materials 323 and 324, respectively.

The coating material 323 used was granulated blue thermoplastic paint containing metallic and mica flakes and was heated to a temperature of 190°C. Such heating rendered the coating material plastic, enabling it to be injected by its extruder into the mould using an injection pressure of around 1300 bar (130 MPa).

The substrate material 324 was white polypropylene and was heated to a temperature of 230°C to enable it to be injected by the second extruder at a pressure of 1300 bar (130 MPa).

Using the injection method as described with reference to Figures 15 to 18 with the mould 310 heated to a temperature of 60°C, the materials 323, 324 were injected into the mould 310. After about 90 seconds the moulded wing 350 was then removed from the mould 310 and inspected.

It was found that the coating material 323 had completely enveloped the substrate 324 leaving no light patches or uncovered areas.

The mould itself did not have mould cavity surfaces of a quality which would enable a high gloss finish to be obtained, as wings normally made in the mould were intended for post-mould painting by spraying or dipping. Nevertheless, the finish obtained with the moulded plastics paint material was extremely good, giving a metallic paint appearance comparable with that normally acceptable on motor vehicle body panels. The moulding demonstrated clearly that a mould cavity having a superfine finish would enable high gloss body panels to be produced by a method in accordance with the invention with no sign whatsoever of the "orange peel" finish characteristic of powder paint coatings applied electrostatically.

The depth d of the paint coating material 323 on the polypropylene substrate material 324 could be controlled by varying the quantities of the materials 323, 324

injected into the mould and it was found that the two materials bonded well to each other, rendering the coating and substrate highly resistant to separation.

The wing 350 was moulded so as to include integral fixing flanges 352, 353 with fastener receiving apertures 352a, 353a therein and a stiffening flange 354. It was found that the paint coating material 323 enveloped the edges of the flanges and the apertures leaving no gaps where the white polypropylene was visible.

It was found that the same results were obtained on repeating the moulding process, and with the vehicle front wing selected for the experiment (suitable for use on a Rover Maestro vehicle) it was found possible to provide wing mouldings at a rate of one wing every 120 seconds.

In Fig. 23, a tubular hollow article 410 is formed by a coextrusion machine 412 of known kind and comprises an inner layer or substrate 413 of plastics material, an intermediate layer 414 of pigmented plastics material to provide a desired colouring, and an outer layer 415 which provides a transparent clear coat.

The substrate material 413 may be a thermoplastics material comprising, for example, polypropylene, a polyamide, ABS, polycarbonate or a blend or alloy of such materials, for example polycarbonate/ABS or polyphenylene oxide/polycarbonate.

The hollow article 410 leaves the extruder 412 in a plastic mouldable condition and is positioned between the mould halves 416, 417 of a mould 418 as shown in Fig. 24.

The mould is then closed as shown in Fig. 25 so that the lower end of the hollow article 410 is pinched together and air indicated by arrow A is introduced into the open upper end of the hollow article. The incoming air inflates the hollow article so that it conforms to the shape of the mould surface indicated at 418a. It

will be noted from Fig. 25 that the outer layer 415 is moved into contact with the mould surface 418a as a result of the inflation, the surface 418a preferably being extremely smooth to provide a high gloss finish on the outer layer 415.

The mould 418 is preferably cool e.g., around 60°C. After the blow moulding stage shown in Fig. 25, the mould remains closed for a length of time sufficient to enable the thermoplastics layer 413, 414 to cool. The mould halves 416, 417 are then separated and the moulded article, indicated by 420 in Fig. 26, is removed. The moulded article shown in Fig. 26 is in the form of a bottle.

If desired, further heat can be applied to the outer layer 415 after the moulded article 420 has been removed from the mould. Such a heating step can help to provide a superfine finish to the outer layer, the outer layer being free to "flow" as it is not in contact with the mould surface 418a.

In Fig. 27, a vehicle 421 has a spoiler 422 attached to the rear end thereof. The spoiler 422 can be formed by, for example, blow moulding as described hereinafter and, as shown in Fig. 28, has an inner layer or substrate 423 and an outer coating layer 424 of paint.

It has been known hitherto to form spoilers by blow moulding, the moulded article comprising a single layer of plastics material to which paint is subsequently applied by spraying or dipping to match the required colour of the vehicle. By using a blow moulding method as described herein, such subsequent painting of the spoiler is rendered unnecessary.

A method of manufacturing the spoiler 422 is now described with reference to Figures 29 to 32.

In Fig. 29, a coextrusion machine 412 of known kind receives plastics material 423a to form a substrate of the spoiler 422 and also receives a coating material,

which in this case is a powdered plastics paint 424a, for providing the desired colour finish for the spoiler.

The material 423a may be a thermoplastics material comprising polypropylene, a polyamide, ABS, polycarbonate, polystyrene or a blend or alloy thereof, for example, a polycarbonate/ABS or polyphenylene oxide/polycarbonate blend or a polypropylene/polyamide alloy.

The substrate material 423a and powdered plastics paint 424a are heated in the extruder 412 and coextruded to produce a hollow article 425 comprising a tubular substrate 423 having an outer layer 424 of paint. The thermoplastics substrate 423 and the paint layer 424 are in a mouldable form immediately after leaving the extruder 412.

The hollow article 425 produced by the extruder 412 is positioned between the mould halves 426, 427 of a mould 428. The mould halves 426, 427 are mounted on respective mountings 429, 430 which themselves are mounted on spaced-apart guides 432 for movement towards and away from each other. The mounting 429 is axially secured to the guides 432 and the mounting 430 is slidable on the guides 432. Spaced-apart fluid-operable actuators 433 act between the mounting 430 and a reaction plate 434 to which the guides 432 are secured. The mounting 429, 430, guides 432 and reaction plate 434 form part of a blow moulding machine of known kind.

Once the hollow article 425 has been positioned between the mould halves 426, 427 shown in Fig. 29, the fluid-operable actuators 433 are extended so as to move the mould halves 426, 427 towards each other until they close as shown in Fig. 30. The hollow article 425 is then inflated by air introduced through a nozzle 435, the air urging the hollow article outwardly towards the inner surface of the mould indicated at 428a. The surface 428a has a superfine finish and the pressure of the air

introduced into the hollow article causes the paint layer 424 to be urged firmly into contact with the surface 428a whereby a high gloss finish is obtained on the outer surface of the paint layer 424 (see Fig. 31).

The mould 428 is cool (e.g. around 60°C). The mould halves 426, 427 are left closed for a sufficient length of time to allow the moulded article to cool sufficiently to be removed from the mould. The mould halves 426, 427 are then separated as shown in Fig. 32 by operating the actuators 433 in the reverse direction. The blow-moulded spoiler 422 can then be removed from the mould. The mould halves 426, 427 have narrow edges 426a, 427a which pinch the ends of the hollow article 425 therebetween and assist in separation of the moulded spoiler from end sections 425a, 425b of the hollow article. The mould halves 416, 417 shown in Figs. 24 and 25 can be similarly formed.

If desired, the spoiler 422 can be made with three layers of plastics material in the same manner as described with the respect to Figs. 23 to 25. In such a case, the outer layer will provide a clear coat 440 (see Fig. 33), the material 423a will be used to form a substrate 423 and a third material 442a in the form of a pigmented plastic material is provided to form an intermediate layer 442 of desired colour. As in Fig. 23, the extruder 412 will produce a hollow member with three layers which is blow moulded to form the spoiler. Where a clear coat 415, 440 is provided, it may contain additives such as free radical scavengers (UV stabilizers) to protect the intermediate layer 414, 442 against the effect of ultraviolet light.

If desired, the powdered plastics paint 424a or the pigmented plastic material 442a may include a flake-like additive such as metallic or mineral flakes 450 (e.g. aluminium or mica flakes) to provide a metallic or sparkle finish. The extrusion of the plastics material

having the flake-like additives tends to cause the flakes 450 to orientate themselves in the paint layer 424 so that they lie generally in a plane parallel with the direction of extrusion and generally parallel with the layer of the plastics material itself. Where the flakes 450 are provided in the paint layer 424, the flakes are constrained to lie within the confines defined by the mould surfaces 428a. Flake-like additives can similarly be used in the method of moulding described with respect to Figs. 23 to 25.

Figs. 35 to 37 show two further articles in accordance with the invention. The article 501 shown in Fig. 35 is in the form of a vehicle bumper which, as shown in Fig. 36, comprises a substrate 502 having a coating 503 thereon. The article 504 shown in Fig. 37 is in the form of a wheel trim comprising a substrate 505 having a coating 506 thereon. If desired, the coating 506 could be thicker on the outer surface of the wheel trim than on the inner surface.

The articles shown in Figs. 35 to 37 can be made by any suitable method, for example, by a dual injection method. Suitable dual injection methods are described, for example, with reference to Figs. 14 to 20.

The following Examples illustrate the invention. In the Examples, percentages are by weight, unless otherwise indicated.

Example 1

A thermoplastic paint composition comprising:
87.1 % polypropylene (Melt index 25.0 g/10 min as measured by ISO 1133 (2.16 kg at 230°C))
10.0 % BaSO₄ filler
2.0 % black pigment
0.5 % antioxidant
0.4 % UV stabiliser

was used in the manufacture of a coated polypropylene

vehicle component (a battery tray). The components of the paint composition were mixed, and the mixture was extruded to form pellets which were cryogenically ground at a mill temperature of -80°C in an Alpine UPZ 160 mill to give a powder having an average particle size of $120\text{ }\mu\text{m}$.

The powder was flame sprayed onto the inside of an open injection mould using a hand-held flame spray gun with a right-angled nozzle and a small gravity feed hopper. The mould was preheated to a temperature of 80 to 100°C . Compressed air was supplied to the gun at a pressure of 2.25 bar (0.225 MPa), giving a powder flow rate of about 25 g/min (about 0.4 g/s). The fuel gases used were oxygen and acetylene.

When the interior of the mould had a continuous coating thereon, the mould was closed and polypropylene substrate material at a temperature of about 200°C was injected into the mould. After partial cooling, the thermoplastic moulded article was removed from the mould and allowed to cool to room temperature. The coating had an average thickness of $150\text{ }\mu\text{m}$. The coating passed the crosshatch adhesion test (BS 3900 E 6/ISO 2409) before and after a 24 hour watersoak with a 0% loss. The coating also passed an environmental cycling (65/U) test (RES 30EE102 Issue 9, which is part of Rover Engineering Standard RES.22.PL.08), humidity test (BS 3900 Part F2 - 168hr), and a power wash (80°C , 80 bar (8 MPa), 1 min (60 sec)) test.

Example 2

This Example illustrates articles formed by compression moulding.

A thermoplastic paint composition comprising:
 79.1 wt. \% polypropylene (as in the paint composition of Example 1)
 20.0 wt. \% white pigment
 0.9 wt. \% antioxidant

was used to apply a paint layer to a sheet of glass fibre-reinforced polypropylene. The paint, in the form of a powder of average particle size 120 μm , was flame sprayed, using the same gun type and gun setting as in Example 1, onto an inner surface of an open compression mould (Hounsell press) preheated to a temperature in the range of 80 to 100°C. When the said inner surface of the mould had a continuous coating thereon, a preheated preform of the substrate sheet was positioned in the mould on the sprayed surface. The mould was then closed, thereby punching out the desired shape. After partial cooling, the moulded article was removed from the mould and allowed to cool to room temperature. The coating, which had an average thickness of 150 μm , was of a high quality.

A coating of high quality, having a thickness of 150 μm , was also obtained when this Example was repeated spraying the coating material onto the substrate material rather than onto the mould surface.

Example 3

99.25 wt. % polyamide/polypropylene alloy sold under the trade name Orgalloy R60ES

0.50 wt. % of carbon black masterbatch

0.25 wt. % of antioxidant

were mixed, extruded and ground as described in Example 1 to give a thermoplastic paint composition having an average particle size of 120 μm . (In the masterbatch, the carbon black was blended with a small amount of polypropylene.) This composition was flame sprayed onto the interior of an injection mould using a flame spray gun as described in Example 1.

When the interior of the mould had a continuous coating thereon, a polyamide-6,6 substrate material, at a temperature of about 250 to 300°C, was injected into the mould. The coating layer in the final thermoplastic

article had an average thickness of 150 μm and was found to adhere well to the substrate material.

Examples 4 to 8

A thermoplastic paint composition comprising:

91.6 % polypropylene (as in the paint composition of Example 1)

2.5 % carbon black masterbatch

0.5 % antioxidant

0.4 % UV stabilizer

5.0 % acrylic-modified polyolefinic ionomer

was used (Example 4) to produce a thermoplastic article (coated substrate) using the general method described in Example 1, polypropylene being used as the substrate material.

In Examples 5 to 7, the acrylic-modified polyolefinic ionomer was replaced by 5 % of a reversibly crosslinkable styrene-ethylene/butylene-styrene rubber sold under the trade name Kraton, a low molecular weight ionomer, and a polyolefinic ionomer, respectively. In Example 8, the polypropylene and acrylic-modified polyolefinic ionomer were replaced by 96.6 % of a polypropylene/polyethylene blend. The substrate material in each of Examples 5 to 8 was polypropylene.

In each of Examples 4 to 8, the article produced included a coating of thickness of not more than 150 μm and having excellent properties. Similar results were obtained when Example 4 was repeated using a mixture of recycled polyolefins as the substrate material.

Example 9

The coating method described in Example 1 was repeated using the same substrate material and the

following coating material:

- 87 % polypropylene (as in the paint composition in Example 1)
- 0.5 % antioxidant
- 0.4 % UV stabilizer
- 4 % finely divided aluminium (average particle size 75 μm)
- 2 % finely divided aluminium (average particle size 200 μm)
- 4.1 % styrene-ethylene/butylene-styrene reversibly crosslinkable rubber.

A thermoplastic article including a metallic coating having a thickness of less than 150 μm and excellent appearance and properties, including EMI shielding properties, was obtained. The finely divided aluminium was well below the exposed surface of the coating, and was thus protected from oxidation.

Example 10

A sample of polypropylene homopolymer in pellet form having a weight average molecular weight Mw of between 200,000 and 280,000 (measured by gel permeation chromatography) and a melt flow index of 25 g/10 minutes measured in accordance with ISO1133 was premixed in a barrel blender with a styrene-ethylene/butylene-styrene cross-linkable rubber, a hindered phenol antioxidant sold under the trade mark Irganox 1010, two UV stabilisers, transparent micaceous titanium dioxide in platelet form, and a mixture of pigments. The proportions of the various components were as follows:

- 63 -

Parts by weight

Polypropylene	2028
Styrene-ethylene/butylene-styrene cross-linkable rubber	250
Irganox 1010	12.5
Green phthalocyanine (BASF L8730)	25
Blue phthalocyanine (BASF L6920)	25
Special Black 4A (Carbon black)	1.35
Supersparkle mica coated with TiO ₂	82.5
Sparkle mica coated with TiO ₂	12.5
Exterior Hi-lite Blue (micaceous TiO ₂ with chromium oxide coating)	50.0
UV stabilizers	13.50

The mixture was extruded using a thermoplastic extruder at 200 rpm with an l/d ratio of 16 at temperature settings of 160°C at the inlet, 160°C in the barrel and 180°C at the diehead. The strand produced at the diehead was quenched in a water bath and pelletized to produce pellets of paint 5 mm in length and 2 mm in diameter.

The pellets were allowed to dry and were loaded into one of the hoppers of a Battenfeld multicomponent injection moulding machine having a mould with a polished interior surface. The other hopper was loaded with pellets of pure polypropylene homopolymer (the substrate material).

The conditions of extrusion were identical to those for the pelletizing first extrusion. The paint material was injected first, at an injection pressure of 1500 bar (150 MPa), followed immediately afterwards by the core material.

The finished part, which was a bumper bar for a vehicle, was ejected from the polished mould without the use of a mould release agent. The coating in the

finished part had a thickness of approximately 300 μm .

The surface of the finished part had a gloss measured by ASTM D523-67, of 90 % at a 60 degree head. On comparison with a standard automotive panel the metallic appearance (imparted by the pearlescent material) was bright and of a class A finish.

The finished part was subjected to and passed the following performance tests.

Adhesion BS 3900/ISO 2409 - pass GtO at 2 mm.

Saltspray ASTM 117B 1000 hours - no cracking or blistering.

QUV weatherometer 313 nm lamp B 500 hours, no cracking or blistering; and not more than 50 % of original gloss lost.

Spotting tests; Petrol, diesel, brake fluid, acetic acid 0.1M, HCl 0.1M.

No colour change on application.

Example 11

A coating material as in Example 10 having the following formulation was prepared in the manner specified in Example 10:

	<u>Parts by weight</u>
Polypropylene	77
Aluminium pigment in protective resin (needle-like particles of 75 μm length)	3
Pearlescent White	2
Scotchlite ⁺ CIS/250 glass beads	10
Crosslinkable rubber as in Example 10	8

⁺ Trade Mark

The substrate material was the same as that used in Example 10. In this Example a wheel trim for a vehicle

was formed in the mould.

The paint material was injected first, followed by the substrate material, using a Battenfeld BMC 2400 2 x 1000 CNC machine. The barrels of the machine and nozzle were heated to a temperature of 230°C.

The paint material was injected at a speed of 90 mm/second at a maximum injection pressure of 170 bar (17 MPa). That was followed immediately by the injection of the substrate material at a speed of 100 mm/second and a maximum injection pressure of 170 bar (17 MPa). The machine was set to start the delivery of substrate material at 50/108ths of the delivery length of the screw in the second extruder 319. The back pressure in both barrels of the machine was from 3 to 5 bar (0.3 to 5 MPa).

The mould temperature was 50°C and the holding pressure was 20 bar (2 MPa).

A thermoplastic article (a wheel trim for a vehicle) including a very satisfactory coating was obtained. The coating, which had a thickness of 130 to 160 µm on the outer face of the article and a thickness of 20 to 40 µm on the inner face of the article, passed the tests indicated in Example 10, the QUV test for Example 11 being carried out for a period of 300 hours. In the coating the aluminium pigment was close to the surface, but was protected by a layer of polymer. The needles of aluminium were orientated in the coating as a result of the extrusion step.

Example 12 (Comparative)

A typical powder coating formulation was prepared by premixing a thermosetting polyester with triglycidyl isocyanurate (TGIC), a flow aid, and benzoin as a degassing aid. The mixture was then extruded on a Werner Pfleiderer extruder at 120°C.

The resultant extrudate was broken into chips which were then ground to a fine powder having a particle size distribution of:

100 % above 15 microns

55 % above 32 microns

0 % above 100 microns

Aluminium powder was dry blended into the mixture or bonded onto the surface of the powder particles. The powder was then applied through an electrostatic gun onto an aluminium panel and heated for 10 minutes at 200°C.

The resultant paint film was exposed to salt spray and QUV as described in Example 10 and was found to deteriorate rapidly. The sparkle effect achieved was of a low quality and the film did not have a Class A automotive finish.

Example 13

A hollow article was extruded using a conventional coextrusion machine. The hollow article had a inner (substrate) layer of polypropylene, an intermediate layer formed from a powdered paint material as described in Example 10 and an outer layer formed from a clearcoat/laquer material.

The hollow article was then inflated and shaped in a Battenfeld blow moulding machine.

The hollow article was positioned in a mould the surface of which had a temperature of 60°C. Air at a temperature of 20°C was then introduced into the hollow article to inflate it and force the walls thereof against the mould surface. After 30 seconds the mould was opened and the moulded thermoplastic article was removed.

The thicknesses of the layers in the final article were:

Substrate layer	1.00 mm
Intermediate pigmented layer	0.10 mm
Clear coat	0.30 mm

In general it was found that, although good coatings were produced in all the Examples of the invention, superior properties were obtained when using coating materials comprising reversibly crosslinkable thermoplastic materials, including thermoplastic alloys.

Example 14

This Example illustrates one method of manufacturing of an ionomer suitable for use in accordance with the invention.

A sample of an acid-grafted polypropylene available under the trade name Polybond 2015 was extruded and pelletized, and the pellets were cryogenically ground into a fine powder. The powder was then blended with 10 % sodium hydrogen carbonate by weight, based on the weight of the acid-grafted polypropylene, using a APU extruder (screw speed 250 rpm; torque 55-60 %; barrel temperature 200 °C) and formed into a plaque which was examined, before and after storage at 200°C for 10 minutes, using an infrared spectrometer. Plaques were also obtained using 1 % and 5 % respectively of sodium hydrogen carbonate (extrusion temperatures 148°C and 185°C respectively). When working on a large scale, blending could be effected in, for example, an extruder, the cryogenic grinding step being omitted.

Infrared measurements showed that the sodium ions neutralised acid groups in the acid-grafted polypropylene to produce ionic crosslinks between the polymer chains. A greater level of crosslinking was obtained when using higher proportions of sodium hydrogen carbonate. The reaction between the salt and the polymer was incomplete after the extrusion step, and the storage step was thus desirable for obtaining complete reaction.

The ionomer produced was particularly suitable for use, in admixture with polypropylene, in a coating material suitable for use with a polypropylene substrate.

CLAIMS:

1. An article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, the coating comprising a thermoplastic reversibly crosslinkable polymeric material.
2. An article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, the coating having a thickness of at most 500 μm and comprising a thermoplastic polymeric material and one or more substances selected from finely divided metallic materials, finely divided pearlescent materials, and UV stabilizers, with the proviso that the coating does not form part of a sheet of material which has been brought as such into contact with the substrate.
3. An article comprising a substantially thermoplastic substrate comprising recycled material, the substrate having a substantially thermoplastic coating of thickness at most 1 mm on at least one surface thereof.
4. An article comprising a substantially thermoplastic substrate having a coating of thermoplastic paint on at least one surface thereof, the article having been made by a process in which a thermoplastic polymeric material for forming the coating and a thermoplastic polymeric material for forming the substrate are introduced into a mould and are shaped into the article by the mould, if necessary with the application of heat, the process including the steps of bringing coating material in softened or molten form into contact with a surface of the mould or the substrate material.

5. An article as claimed in any one of claims 1 to 4, made by a process including the step of bringing coating material in molten form into contact with a surface of the mould.

6. An article as claimed in any one of claims 1 to 5, made by a process in which coating material is applied to a surface of the mould or the substrate material using flame spraying apparatus.

7. An article as claimed in any one of claims 1 to 5, formed by a multiple-injection process.

8. An article as claimed in any one of claims 1 to 4, formed by a process which includes a blow moulding step.

9. An article as claimed in any one of claims 1 to 3, made by a process which includes a coextrusion step.

10. An article as claimed in any one of claims 1 to 9, which is a vehicle component.

11. An article which comprises a recyclable vehicle component comprising a substantially thermoplastic substrate comprising recycled material, the substrate having a thermoplastic paint coating on at least one surface thereof.

12. A method of manufacturing an article comprising a substrate having a coating on at least one surface thereof, wherein a polymeric coating material and a polymeric substrate material are introduced into a mould and are shaped in the mould to produce the article, if necessary with the application of heat, the coating

being formed by spraying the coating material onto a surface under conditions such that substantially all the coating material is in a softened or molten condition before it contacts the said surface.

13. A method as claimed in claim 12, wherein the coating material is sprayed onto the surface by flame spraying.

14. A method of manufacturing an article comprising a substrate having a coating on at least one surface thereof, wherein a polymeric coating material and a polymeric substrate material are introduced into a mould and are shaped in the mould to produce the article, if necessary with the application of heat, the coating being formed by flame spraying the coating material onto a surface.

15. A method as claimed in any one of claims 12 to 14, wherein the surface onto which the coating material is sprayed is a surface of the mould.

16. A method as claimed in any one of claims 12 to 14, wherein the surface onto which the coating material is sprayed is a surface of the substrate material.

17. A method as claimed in any one of claims 12 to 14, wherein the surface onto which the coating material is sprayed is a support surface and the coating material forms a coherent layer on the surface, the coherent layer being removed from the surface and positioned in the mould in contact with a surface thereof.

~~18.~~ A method as claimed in any one of claims 12 to 17, wherein the polymeric coating material is thermoplastic.

19. A method as claimed in any one of claims 12 to 18, wherein the polymeric substrate material is thermoplastic.

20. A method of manufacturing an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, wherein a polymeric material for forming the coating is heated to a plastic condition and is injected into a mould, a polymeric material for forming the substrate is heated to a plastic condition and is injected into the mould, and the coating material and substrate material are shaped in the mould to produce the article, if necessary with the application of heat, the coating material comprising (a) one or more substances selected from finely divided metallic materials, finely divided pearlescent materials, and UV stabilizers and the method being carried out such that the coating has a thickness of at most 500 μm , and/or (b) at least one thermoplastic reversibly crosslinkable polymeric material.

21. A method as claimed in claim 20, wherein the coating material is injected into the mould substantially simultaneously with the substrate material.

22. A method as claimed in claim 20 or claim 21, wherein the coating material is heated to a temperature above the softening range of the thermoplastic polymeric material before being injected into the mould.

23. A method as claimed in any one of claims 20 to 22, wherein the coating material is heated to a plastic condition in a chamber, which is preferably an extruder barrel, and is injected into the mould through an aperture having an internal diameter smaller than the internal diameter of the chamber.

24. A method as claimed in claim 23, wherein the internal diameter of the aperture is less than 75 %, preferably less than 50 %, of the internal diameter of the chamber.

25. A method as claimed in claim 23 or claim 24, wherein the coating material passes from the chamber to the aperture via a channel having a diameter smaller than the internal diameter of the chamber.

26. A method as claimed in any one of claims 20 to 25, wherein the coating material and substrate material are injected into the mould using a multibarrel injection machine.

27. A method as claimed in claim 26, carried out by dual injection.

28. The use of a heating chamber having an exit aperture of internal diameter or internal cross-section less than the internal diameter or internal cross-section of the chamber to enhance the orientation of a finely divided relatively infusible material in a thermoplastic coating forming part of an article comprising a substrate having a substantially thermoplastic coating on at least one surface thereof, the article being made by a method in which a polymeric material for forming the coating is heated in a heating chamber to a plastic condition and is injected through an aperture into a mould, and a

polymeric material for forming the substrate is heated to a plastic condition and is injected into the mould, and the coating material and substrate material are shaped in the mould to produce the article, the coating material comprising a finely divided relative infusible material the particles of which have one or two dimensions substantially greater than the other two or one.

29. A method of manufacturing an article comprising a substantially thermoplastic substrate having a substantially thermoplastic coating on at least one surface thereof, wherein a hollow article comprising a layer of substrate material and a layer of coating material is positioned in the mould and a fluid is introduced into the hollow article to force the article into contact with the mould, heat being applied if necessary, the coating material comprising (a) one or more substances selected from pigments, finely divided metals, finely divided pearlescent materials, and UV stabilizers, and/or (b) at least one thermoplastic reversibly crosslinkable polymeric material.

30. A method as claimed in claim 29, wherein the hollow article is formed by extrusion.

31. An article or method as claimed in any one of claims 1 and 4 to 30, wherein the coating has a thickness of at most 1 mm.

32. An article or method as claimed in any one of claims 1 and 4 to 30, wherein the coating has a thickness of at most 500 μm .

33. An article or method as claimed in any one of claims 1 to 30, wherein the coating has a thickness of less than 200 μm , for example less than 100 μm .

34. An article or method as claimed in any one of claims 1 to 33, wherein the coating comprises a finely divided relatively infusible material.

35. An article or method as claimed in claim 34, wherein the finely divided relatively infusible material is electrically conductive.

36. An article or method as claimed in claim 34 or claim 35, wherein the finely divided relatively infusible material comprises a metallic material.

37. An article or method as claimed in claim 36, wherein the metallic material is aluminium or stainless steel.

38. An article or method as claimed in any one of claims 1 to 37, wherein the coating is electrically conductive.

39. An article or method as claimed in any one of claims 34 to 38, wherein the finely divided relatively infusible material comprises a pigment.

40. An article or method as claimed in any one of claims 34 to 39, wherein the finely divided relatively infusible material comprises a pearlescent material.

41. An article or method as claimed in any one of claims 1 to 40, wherein the coating forms a thermoplastic paint layer.

42. An article or method as claimed in any one of claims 1 to 40, wherein the article has electromagnetic shielding characteristics.

43. An article or method as claimed in any one of claims 1 to 42, wherein the coating comprises a UV stabilizer and, preferably, a pigment, such that the coating passes the QUV test as defined herein.

44. An article or method as claimed in any one of claims 1 to 43, wherein the coating has an abrasion resistance such that it passes a Taber test as specified in ASTM D1044 (250 cycles).

45. An article or method as claimed in any one of claims 1 to 44, wherein the coating has an impact resistance of at least 2J measured by BS 3900, 1973, Part E3.

46. An article or method as claimed in any one of claims 1 to 45, wherein the coating has a class A automotive finish.

47. An article or method as claimed in any one of claims 1 to 46, wherein the coating material comprises a thermoplastic polymeric material compatible with the thermoplastic polymeric substrate material.

48. An article or method as claimed in any one of claims 2 to 47, wherein the coating material comprises a thermoplastic reversibly crosslinkable polymeric material.

49. An article or method as claimed in any one of claims 2 to 47, wherein the coating material comprises a minor proportion of a thermoplastic reversibly crosslinkable material and a major proportion of another thermoplastic material.

50. An article or method as claimed in claim 48 or claim 49, wherein the reversibly crosslinkable material is an ionomer.

51. An article or method as claimed in claim 48 or claim 49, wherein the reversibly crosslinkable material is a thermoplastic elastomer.

52. An article or method as claimed in any one of claims 1 to 47, wherein the coating material comprises a thermoplastic alloy.

53. An article or method as claimed in any one of claims 1 to 52, wherein the polymeric substrate material comprises a homo- or copolymer of propylene.

54. An article or method as claimed in any one of claims 1 to 53, wherein the polymeric coating material comprises a homo- or copolymer of propylene.

55. An article or method as claimed in any one of claims 1, 2 and 4 to 54, wherein the substrate material comprises recycled material.

56. An article or method as claimed in any one of claims 1 to 55, wherein the coating material comprises a blend of (a) at least one polymer compatible with the substrate material and/or at least one polymer in which the majority of the repeating units are the same as the majority repeating units in the substrate material and (b) at least one polymer which modifies the properties of the coating.

57. An article manufactured by a method as claimed in any one of claims 12 to 19, and 31 to 56, so far as they are dependent on any of claims 12 to 19.

58. An article manufactured by a method as claimed in any one of claims 20 to 27, and 31 to 56, so far as they are dependent on any of claims 20 to 27.

59. An article manufactured by a method as claimed in any one of claims 29, 30, and 31 to 56, so far as they are dependent on claim 29 or claim 30.

60. An article comprising a polymeric substrate having thereon a coating comprising a major proportion of a propylene homo- or copolymer and a minor proportion of an ionomer.

61. An article comprising a substrate comprising a propylene homo- or copolymer, the substrate having thereon a coating comprising a major proportion of a propylene homo- or copolymer and a minor proportion of an ionomer.

62. An article as claimed in any one of claims 1 to 11 and 31 to 61 which is a vehicle component.

63. An article as claimed in claim 62, which is recyclable.

64. A recyclable vehicle component which is an article as claimed in any one of claims 1 to 11 and 31 to 61 made of melt-processable materials.

65. An article as claimed in any claim herein and substantially as described herein.

66. A method as claimed in any claim herein carried out substantially as described herein.

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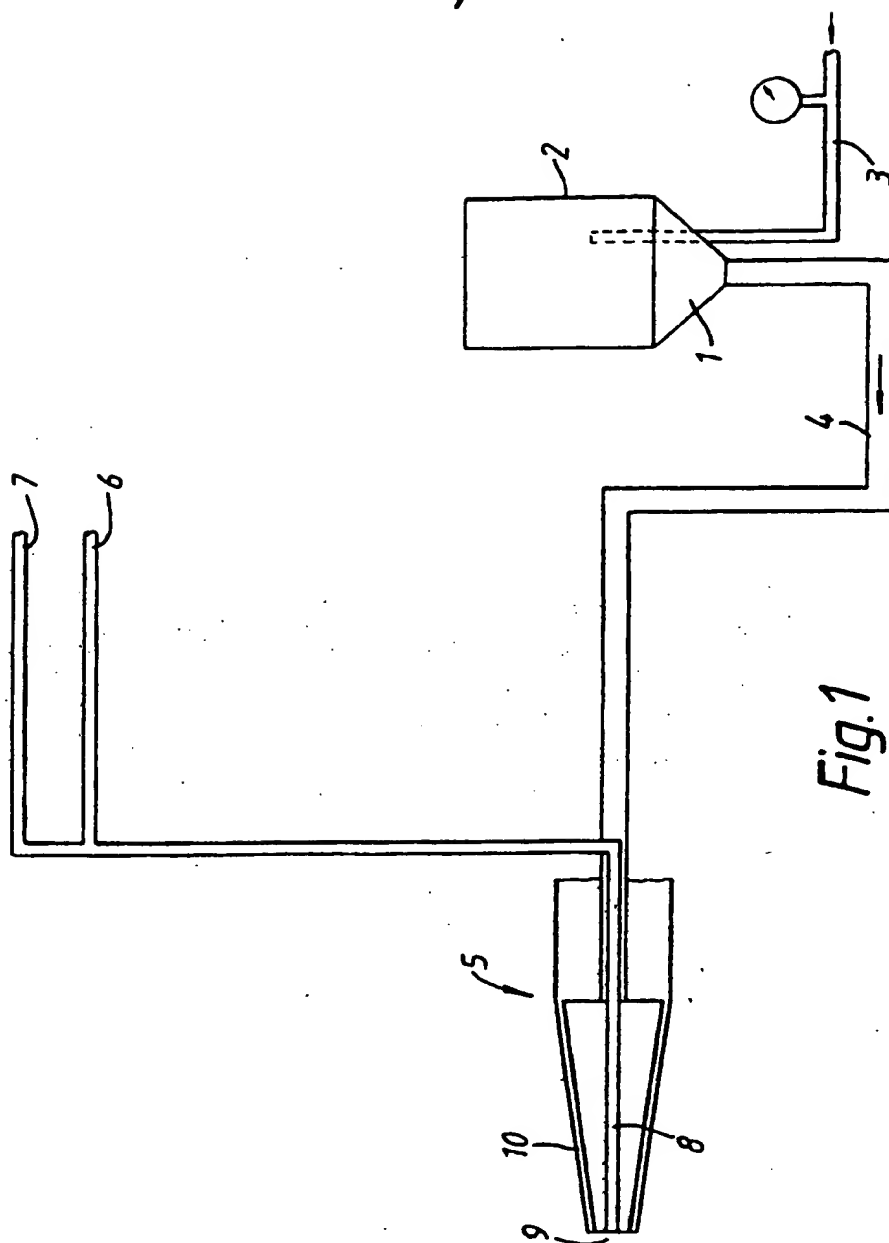


Fig.1

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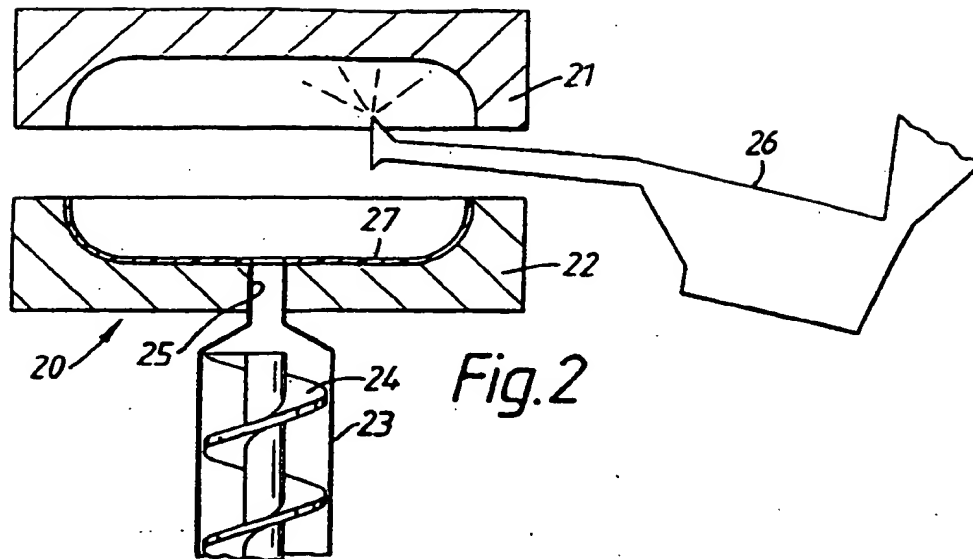


Fig. 2

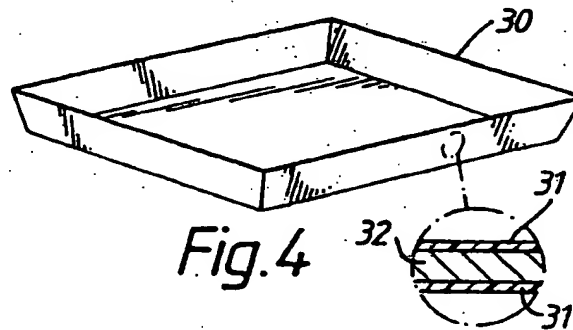


Fig. 4

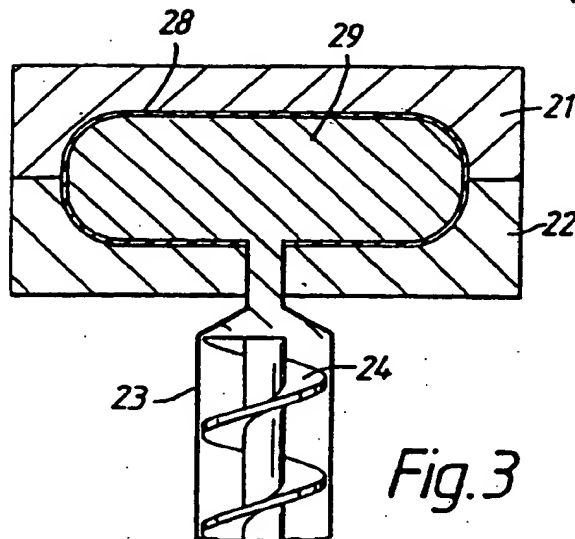


Fig. 3

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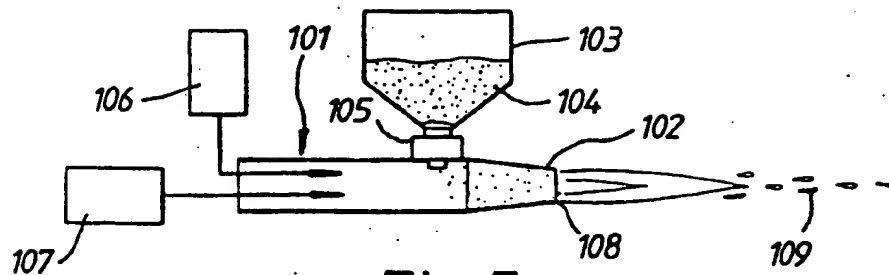


Fig.5

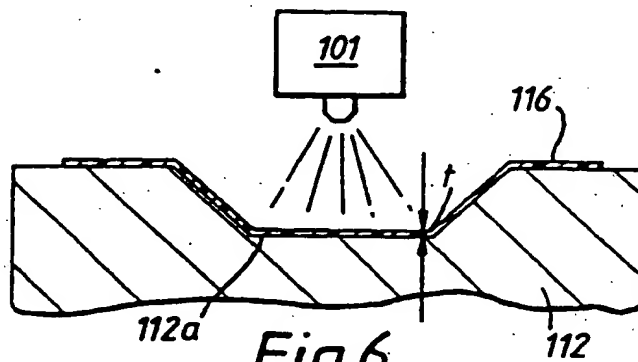


Fig.6

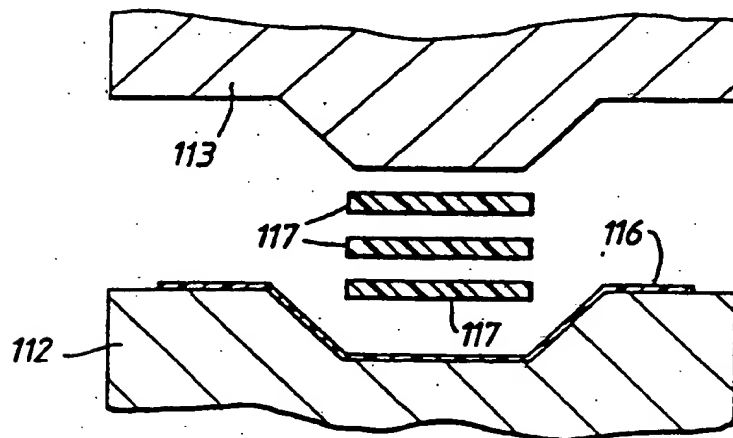


Fig.7

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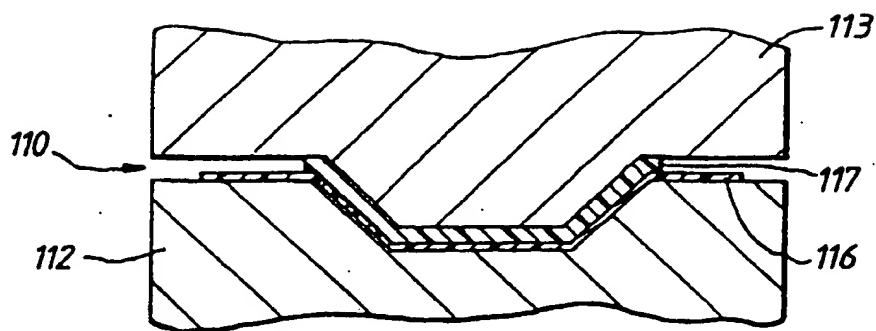


Fig. 8

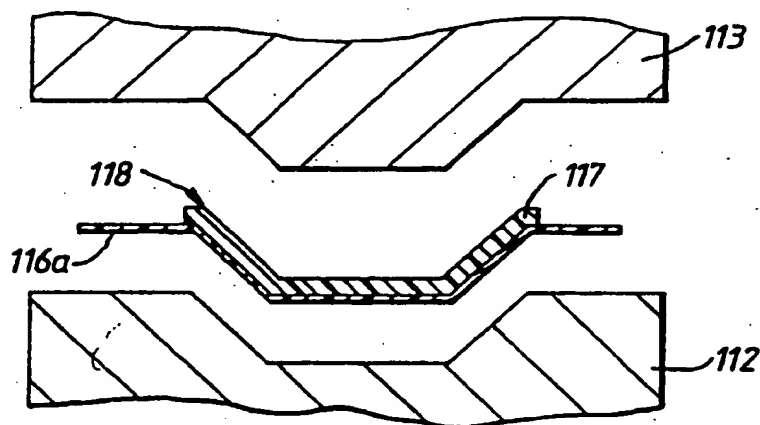


Fig. 9

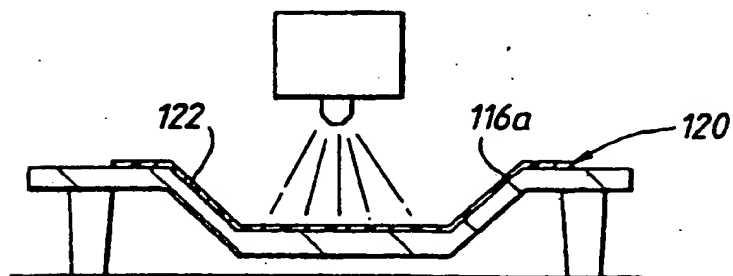


Fig. 10

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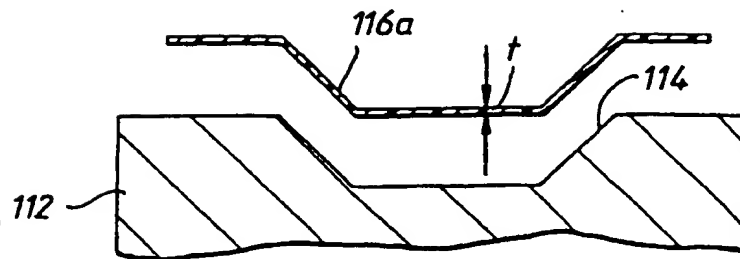


Fig.11

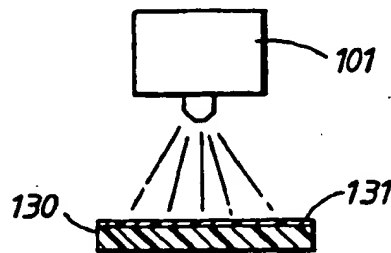


Fig.12

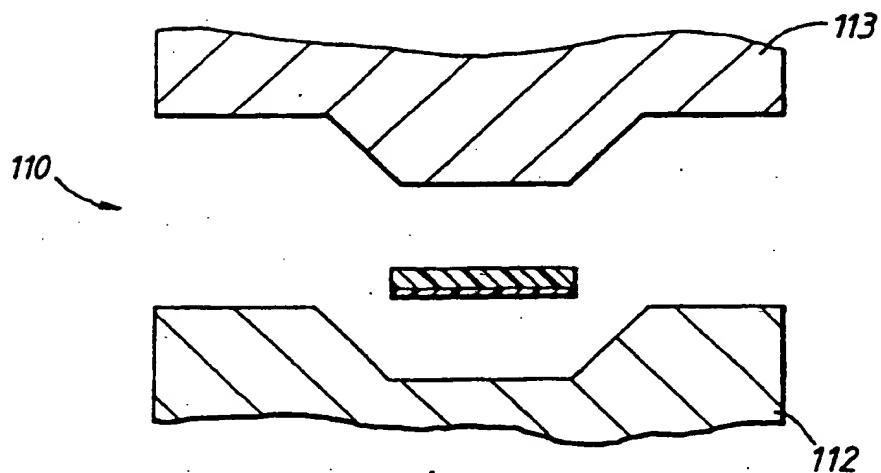
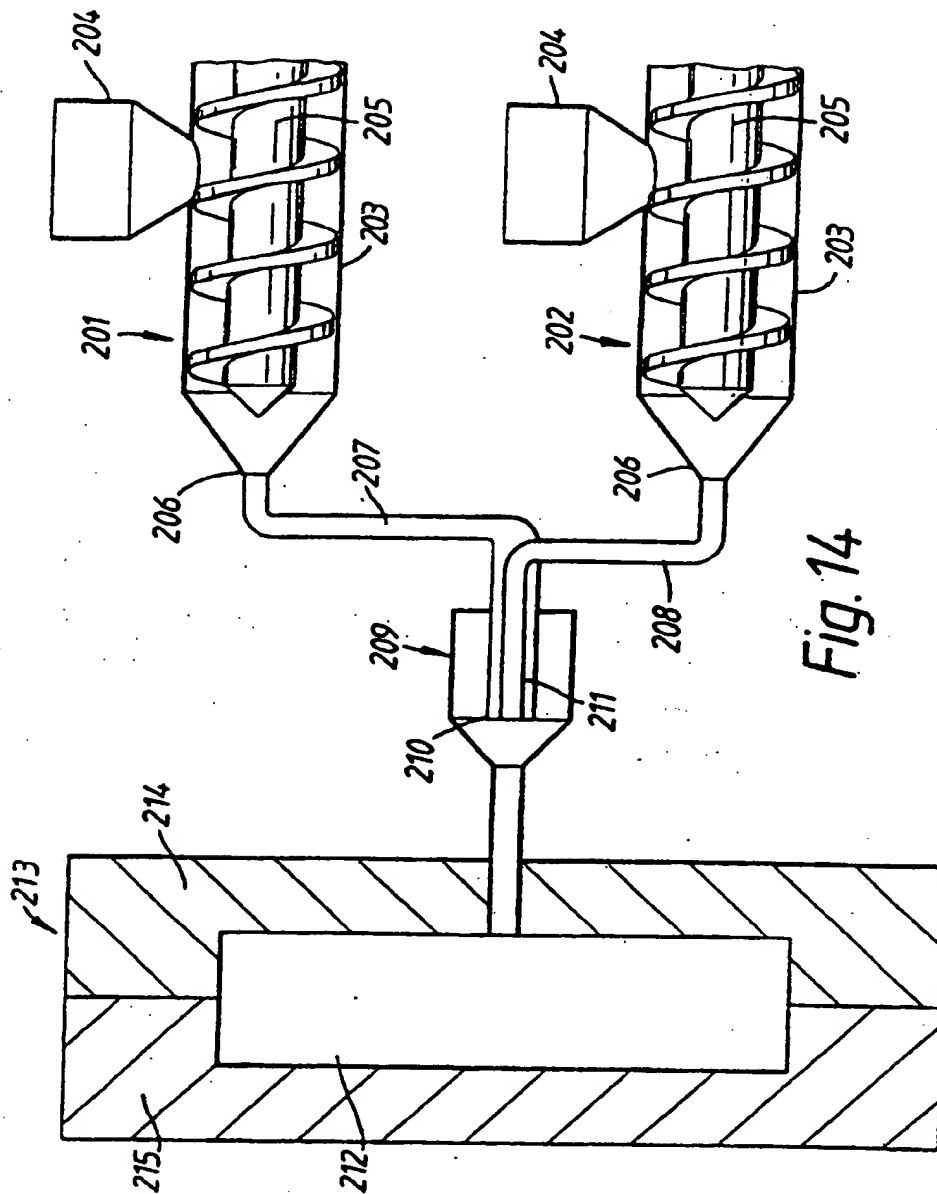


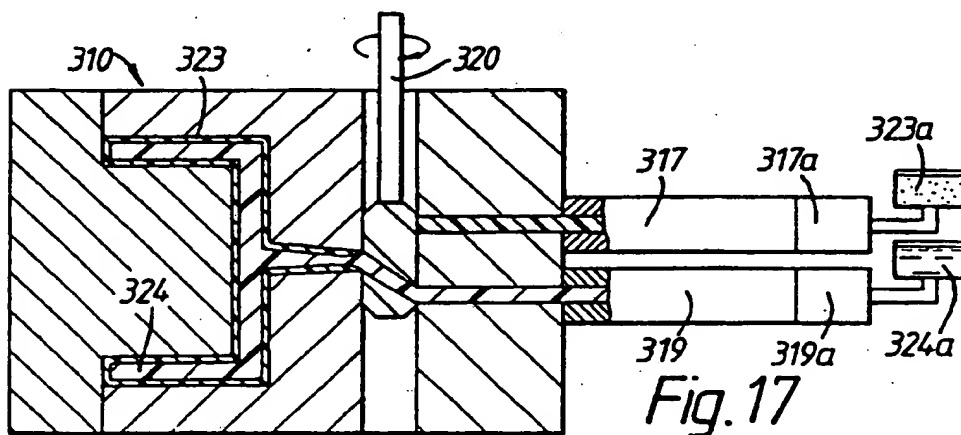
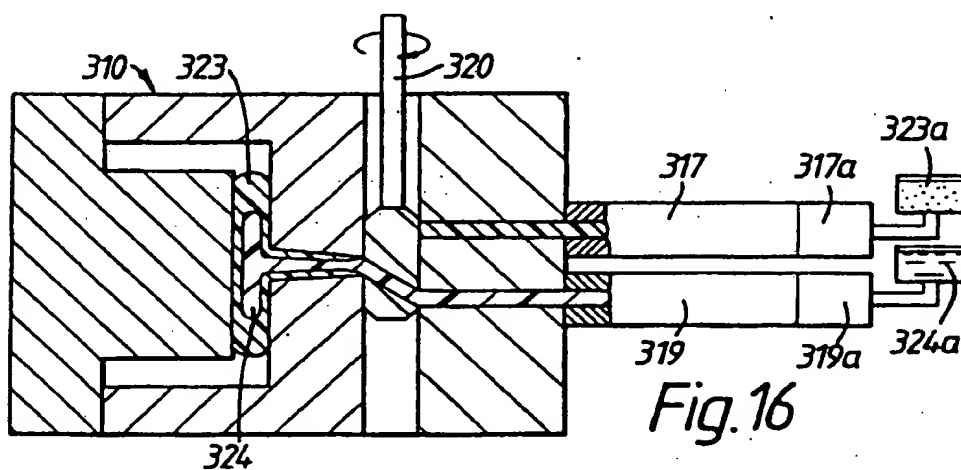
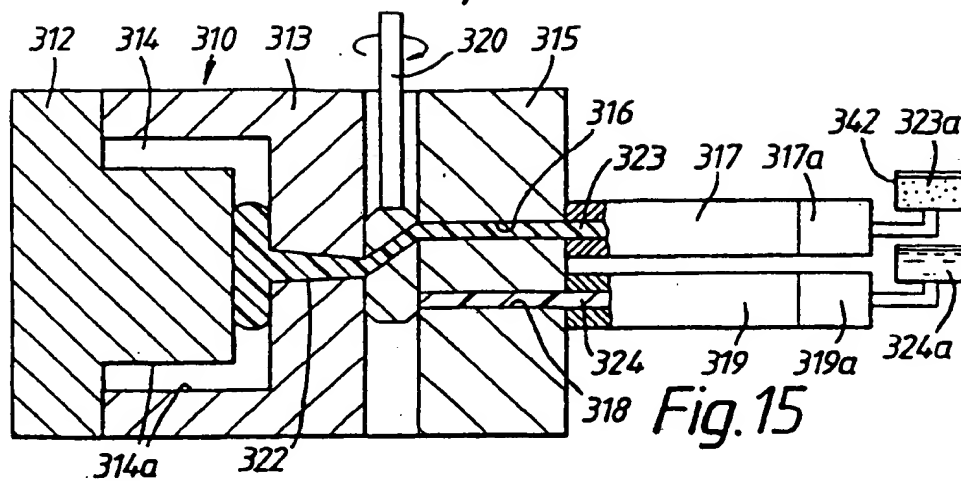
Fig.13

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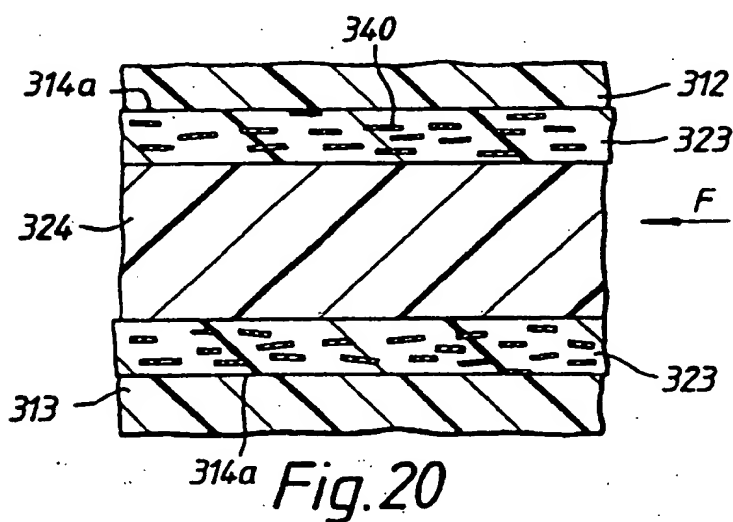
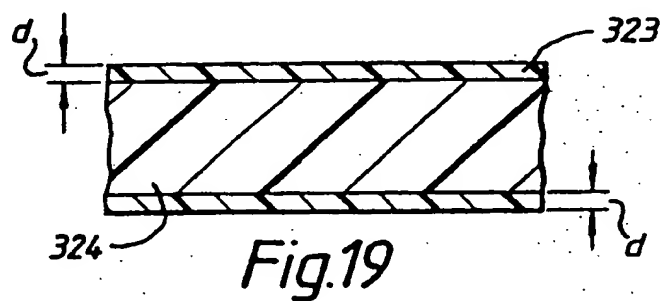
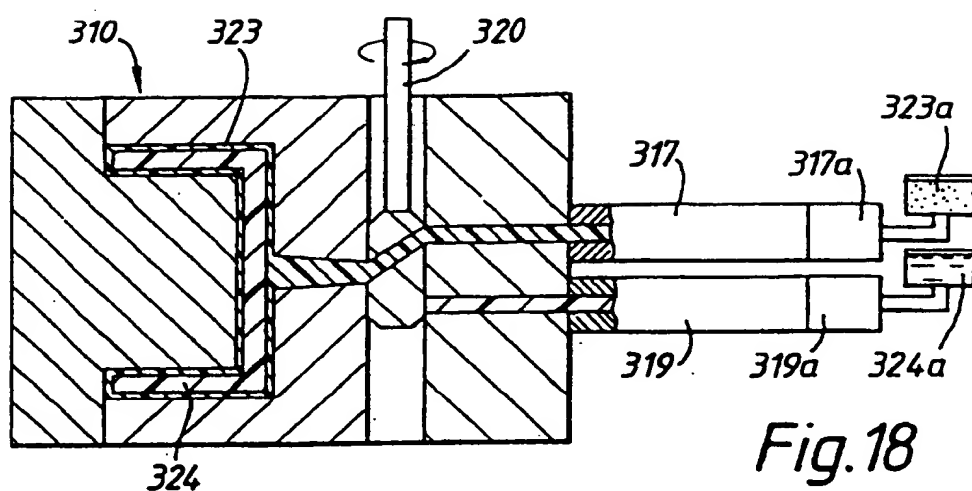


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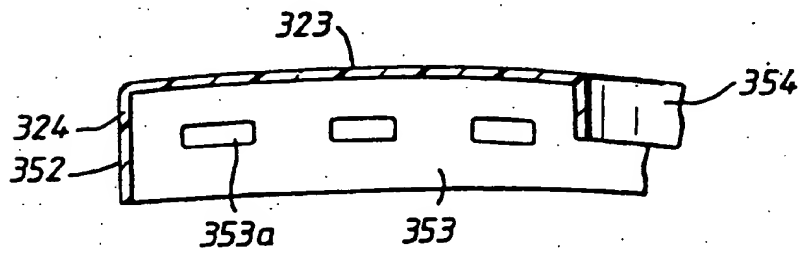
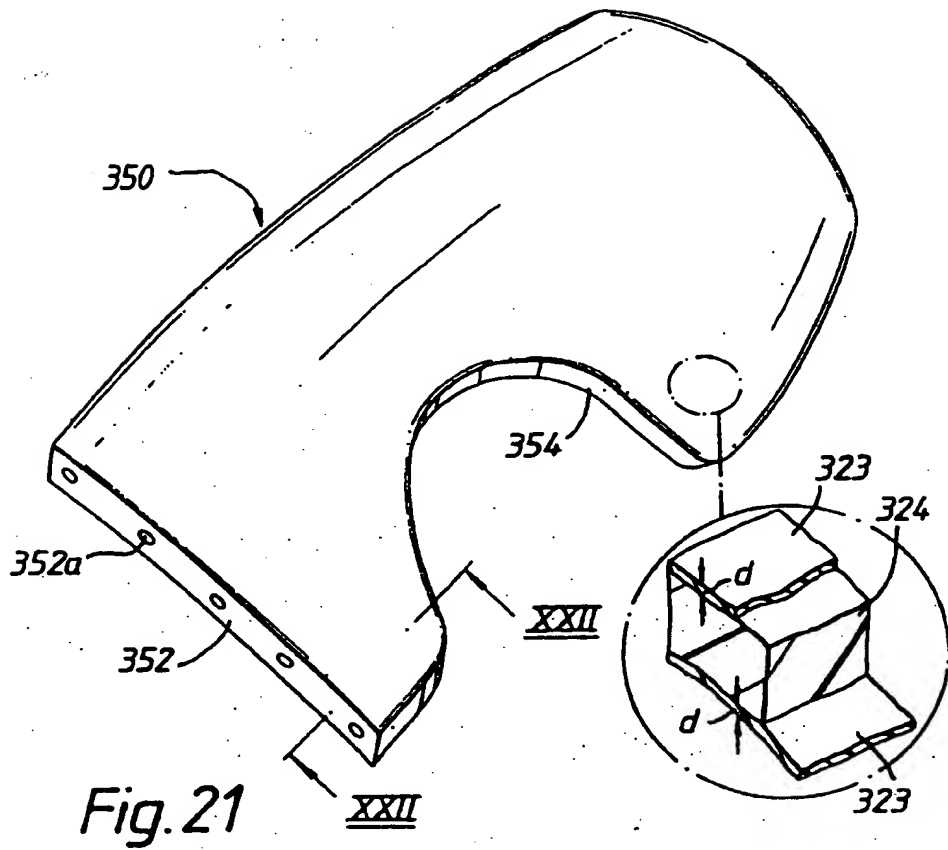
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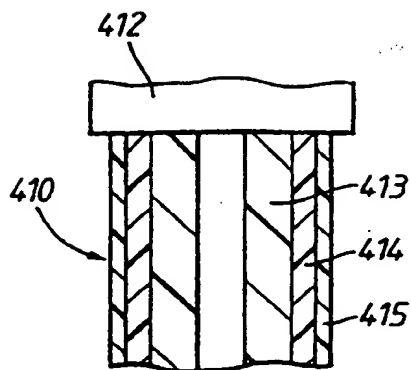


Fig. 23

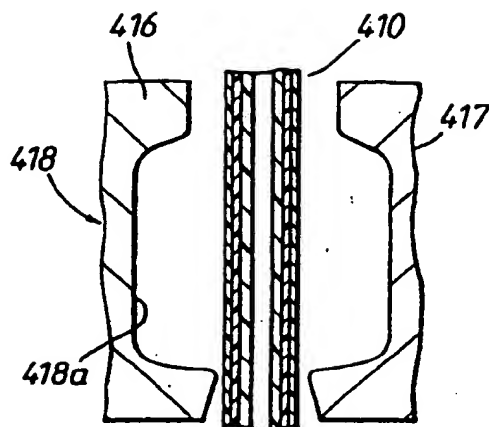


Fig. 24

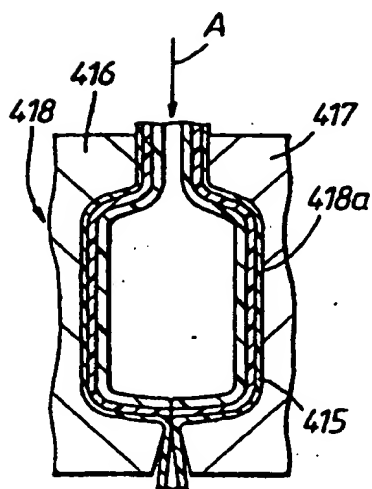


Fig. 25

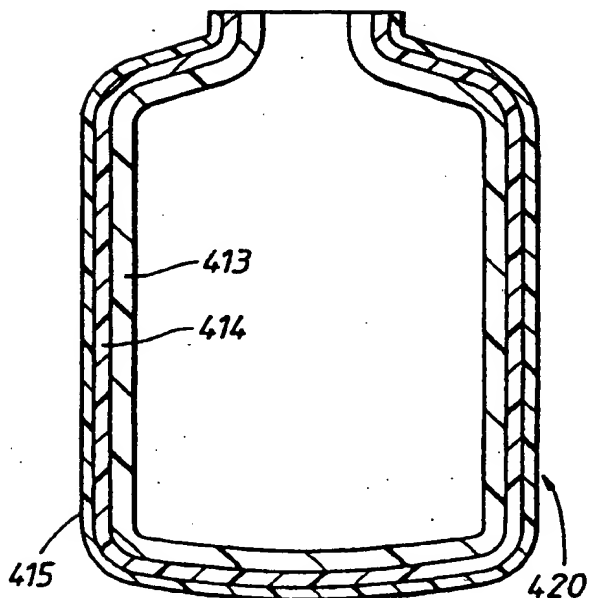


Fig. 26

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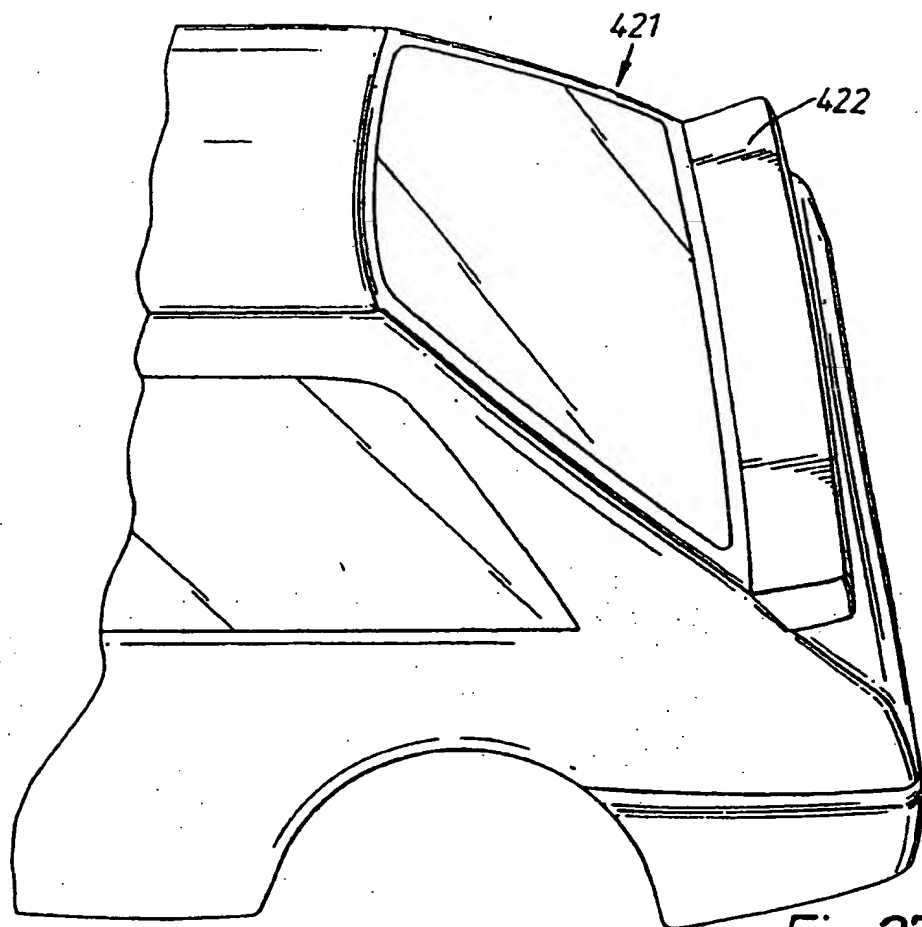


Fig. 27

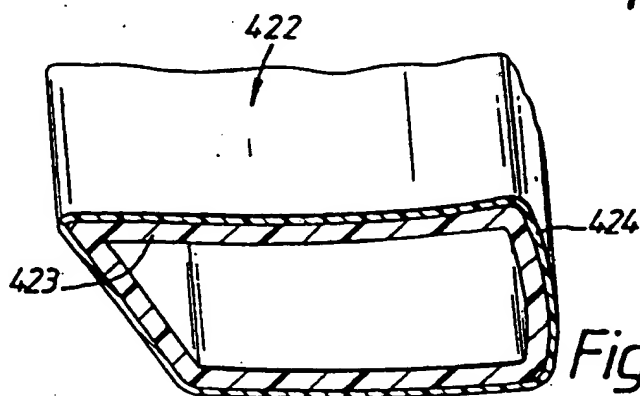


Fig. 28

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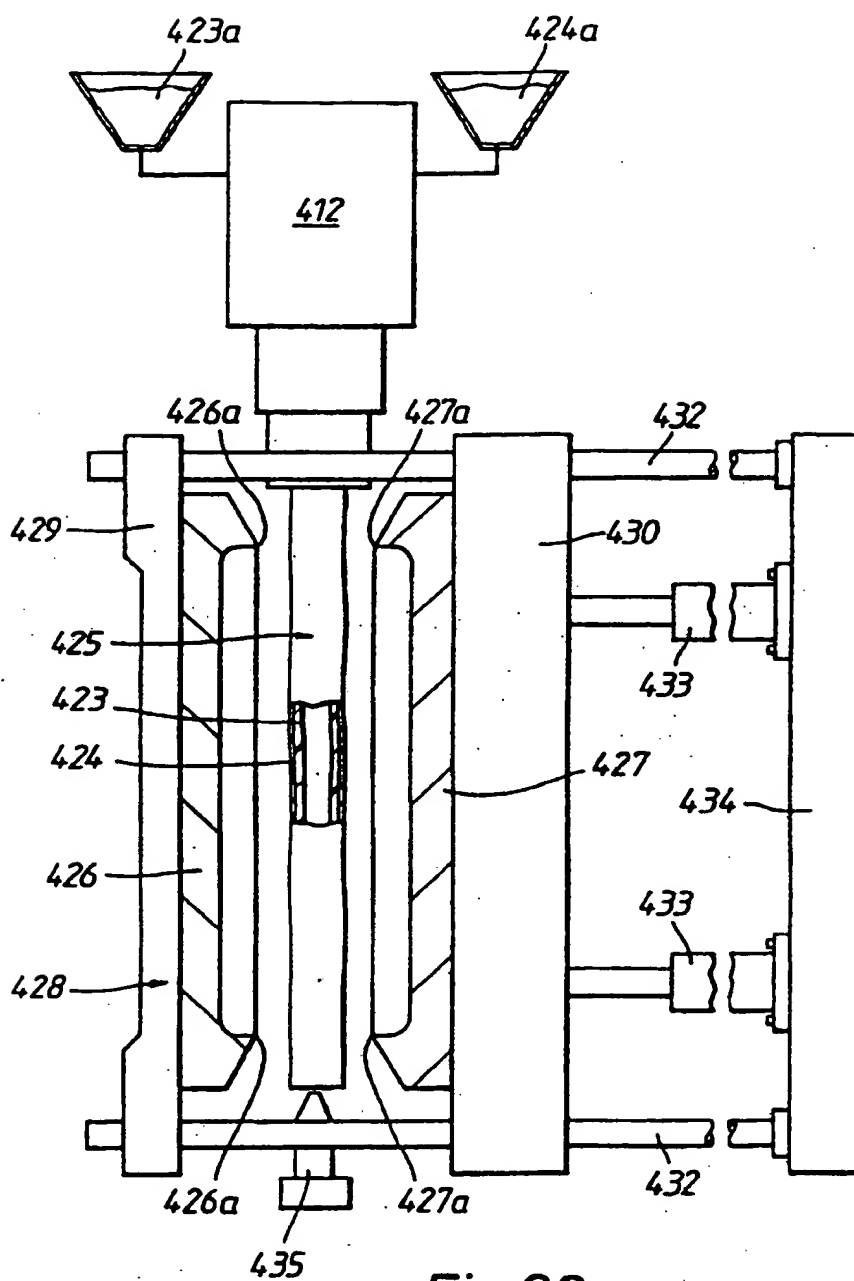


Fig.29

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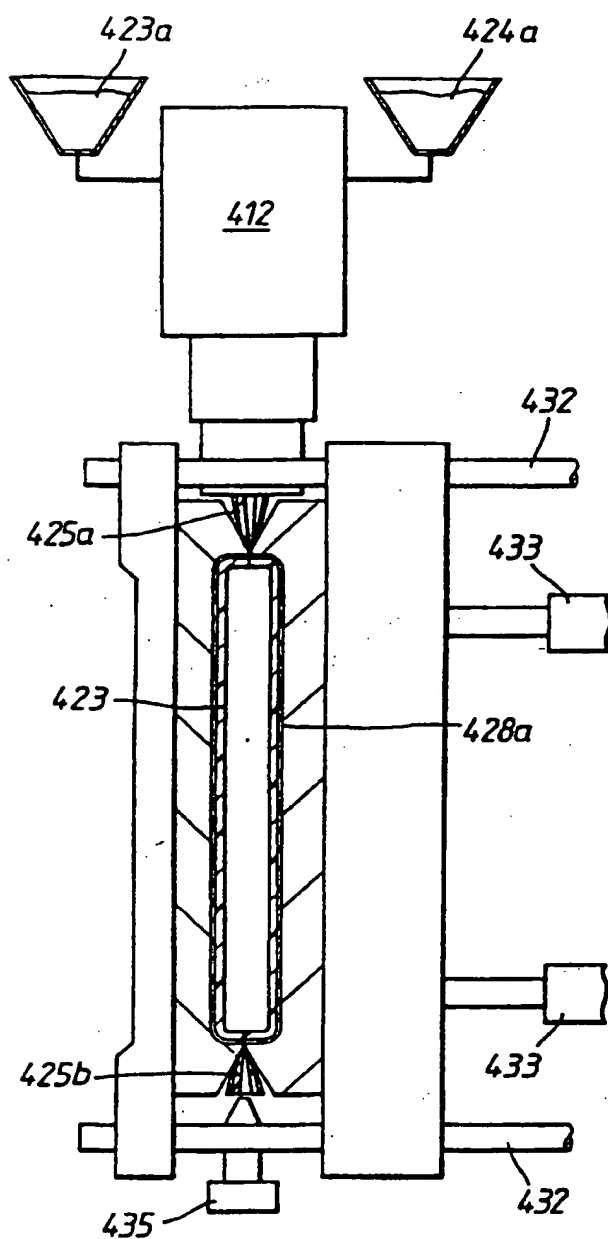


Fig.30

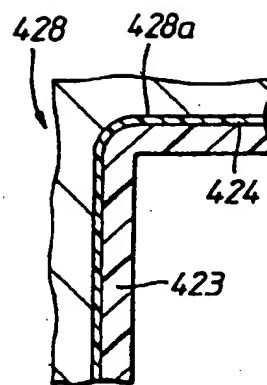


Fig.31

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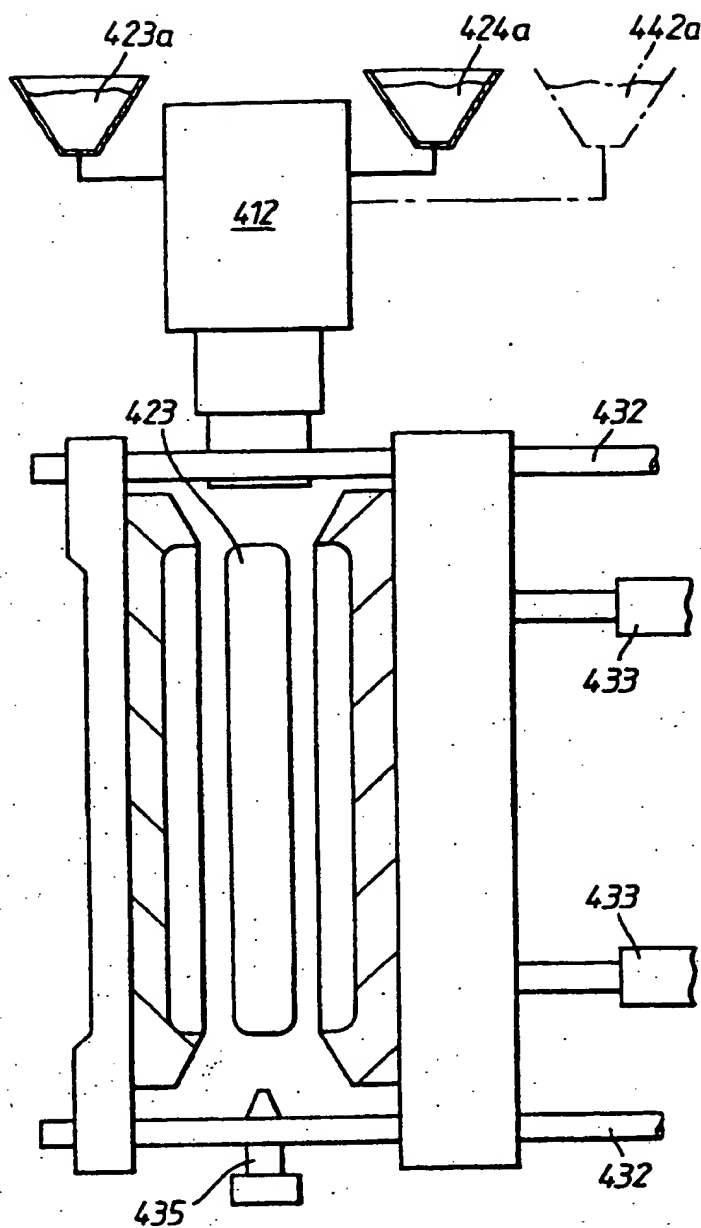
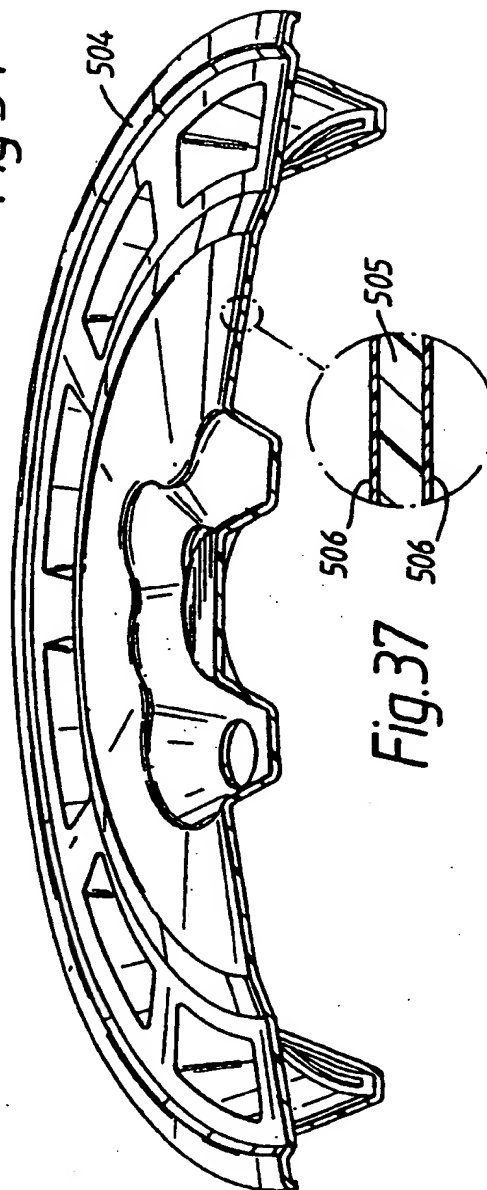
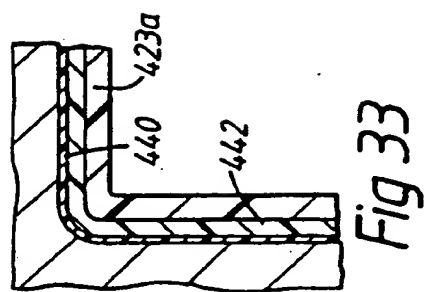
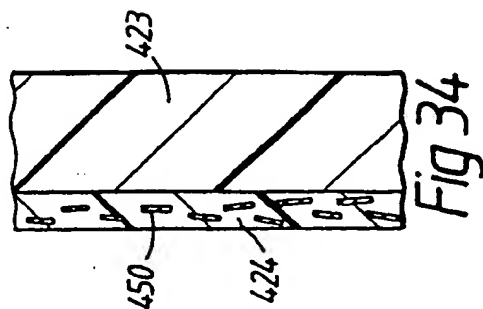


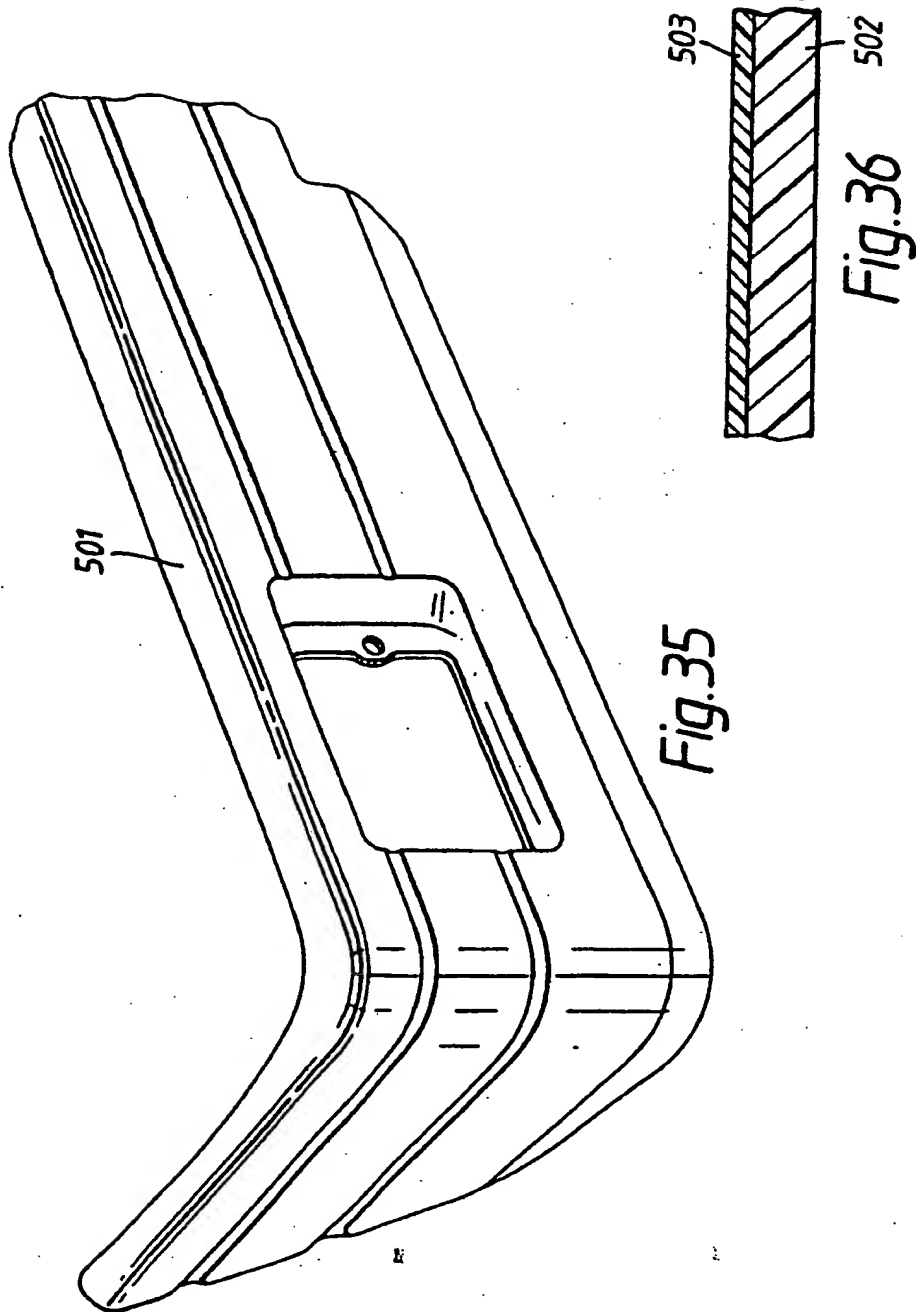
Fig.32

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INTERNATIONAL SEARCH REPORT

 Interx : Application No
 PCT/GB 93/01997

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 B29C37/00 B29C41/08 B29C41/22 B29C45/16 B29C47/06
 B29C49/04 //B29K23:00, B29K77:00, B29K96:00, B29K105:06, B29L9:00,
 B29L31:30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 5 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 89-319128 & JP,A,1 235 635 (TORAY IND INC) 20 September 1989	1,2,4, 7-10, 20-34, 39,41, 43-54, 56-59, 62-66
Y	see abstract	6,11-19, 35-38, 40,42,55
X	PLASTIQUES MODERNES ET ELASTOMERES vol. 43, no. 10, December 1991, PARIS FR pages 64 - 66 'BI-INJECTION: UNE TECHNIQUE OUBLIEE'	3
Y A	see the whole document	11,55 20-28

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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 NL - 2280 HV Rijswijk
 Td. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. Application No

PCT/GB 93/01997

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